Chapter 3B: Mercury and Sulfur Monitoring, Research and Environmental Assessment in South Florida

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SUMMARY

As a highly toxic form of mercury that bioaccumulates in food chains, methylmercury (MeHg) is a risk to wildlife and humans that consume Everglades fish. Sulfur in the form of sulfate increases the rate of MeHg production and may promote phosphate releases from sediments; sulfur in the form of sulfide is toxic to aquatic plants and animals. Regional effects of elevated mercury and sulfur concentrations are evident — and the Everglades has among the highest mercury levels in fish in Florida. Options for reducing these levels include mercury and sulfur source reduction, although the predominant remaining mercury source to the Everglades may be atmospheric deposition from international sources.

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To address these concerns, the Florida Department of Environmental Protection (FDEP) and the South Florida Water Management District (SFWMD or District) are continuing coordinated efforts to better understand the regional sources, transformations, and toxicity of mercury and sulfur. In addition, the Florida Fish and Wildlife Conservation Commission has complementary fish and wildlife programs that monitor for mercury. This chapter updates the status of mercury and sulfur science in South Florida and highlights the progress on research findings. In addition to largemouth bass (LMB) (*Micropterus salmoides*) monitoring, this year's chapter looks more broadly at historical mercury levels and related trends in wildlife including the American alligator (*Alligator mississippiensis*), the Florida panther (*Puma concolor coryi*), and the invasive Burmese python (*Python molurus bivittatus*). In combination with Appendices 3B-1 and 5-6 of this volume, this chapter meets the Everglades Forever Act (EFA) requirement that the District and the FDEP shall annually issue a peer-reviewed report that summarizes all data and findings of mercury research and monitoring in South Florida. Additional detailed scientific information can be found in mercury chapters of the 1999 Everglades Interim Report, 2000–2004 Everglades Consolidated Reports, and 2005–2010 South Florida Environmental Reports.

KEY FINDINGS OF RESEARCH AND MONITORING

- In the Water Conservation Areas over the past 20 years, there has been a significant decline in annual median total mercury concentration in largemouth bass, based on annual monitoring. Mercury in LMB declined 62 percent from a peak level of 1.6 parts per million [(ppm) or milligrams per liter (mg/L)] in 1991 to 0.6 ppm in 2009. Over the past decade, median mercury levels in LMB have varied little, ranging from 0.4 to 0.6 ppm. Still, present concentrations in LMB average twice the U.S. Environmental Protection Agency's recommended human health criterion for fish consumption.
- In the Shark River Slough region of Everglades National Park over the past 20 years, there has been no significant trend in annual median mercury concentration in LMB. This indicates continued favorable conditions for MeHg production and bioaccumulation. In 2010, the median mercury concentration in LMB was 1.4 ppm, which markedly exceeds both federal wildlife protection and human health criteria.
- About 60 percent of the Everglades marsh area has sulfate concentrations that exceed the restoration goal of 1 ppm in surface waters; 1 to 2 ppm of sulfate may represent a threshold level below which mercury methylation rates are relatively low. Further research is needed to quantify sulfur sources and better understand sulfur-related effects on the Everglades ecosystem.
- A regional sulfur mass balance study is under way to quantify the exchange of sulfur between Lake Okeechobee, the Everglades Agricultural Area (EAA), and Water Conservation Areas 1 and 2. Preliminary results suggest that during periods of normal or high rainfall, the EAA is a key source of sulfur to the downstream Everglades, mostly due to sulfur release from soil oxidation, as well as agricultural sulfur application and runoff.

MERCURY IN EVERGLADES WILDLIFE AND FISH

HISTORICAL MONITORING OF MERCURY IN BIOTA

The highly bioaccumulative form of mercury, methylmercury (MeHg), is a concern due to the neurotoxic threat it poses for Everglades wildlife and humans who consume Everglades fish. Elevated levels of mercury (Hg) in biota in Florida were first reported by Ogden (1974) for the Everglades National Park (ENP or Park), and by Bigler et al. (1985) for peninsular Florida. In 1988, reports of mercury levels in largemouth bass (LMB) (*Micropterus salmoides*) in the Everglades Protection Area's (EPA) Water Conservation Areas (WCAs) exceeding 1 part per million (ppm) [1 ppm = 1 milligram per kilogram (mg/kg) or 1 microgram per gram (µg/g)], prompted expanded sampling of fish and wildlife by state environmental and health agencies.

Statewide sampling determined that mercury in LMB was highest in the Everglades, and mercury levels in American alligators (*Alligator mississippiensis*), softshell turtles (*Apalone ferox*), and the endangered Florida panther (*Puma concolor coryi*) were also elevated (Ware et al., 1990).

Since then, mercury has remained a chronic water quality problem in the EPA, the Greater Everglades, and for the remainder of Florida, impacting humans and fish-eating wildlife. High mercury concentrations in fish have not only been documented in the freshwater reaches of the EPA (Loftus et al., 1998; Gabriel et al., 2010a), but also downstream in Florida Bay (Strom and Graves, 2001; Evans et al., 2003) and the Gulf of Mexico (Adams et al., 2003).

In response to findings that mercury concentrations in sport fish exceeded human health criteria, the Florida Department of Health (FDOH) issued fish consumption advisories for Florida Bay, the Gulf of Mexico, the Atlantic, and the fresh waters of the ENP, WCAs, and numerous lakes and rivers (FDOH, 2009). In addition, one wildlife species, the pig frog (*Rana grylio*), has a limited-consumption advisory (FDOH, 2008), and the Florida Fish and Wildlife Conservation Commission (FWC) has banned the sale of alligator meat harvested from the Francis S. Taylor Wildlife Management Area (Francis S. Taylor WMA), which overlaps Water Conservation Area 3B.

Fish and wildlife monitoring is necessary to (1) assess human and wildlife risks from consumption of mercury-contaminated fish, (2) describe spatial and temporal trends in mercury bioaccumulation, and (3) gain a better understanding of the ecological significance of mercury bioaccumulation in fish and wildlife. The following are summaries of research on the status and trends of mercury in the American alligator, Florida panther, and the nonindigenous invasive Burmese python (*Python molurus bivittatus*) (**Figure 3B-1**). In addition, this chapter reports on fish sampling activities within the Greater Everglades.

Figure 3B-1. Fish and wildlife species in the Everglades region, including (clockwise from left) the native American alligator (*Alligator mississippiensis*), invasive Burmese python (*Python molurus bivittatus*), Florida panther (*Puma concolor coryi*), and largemouth bass (LMB) (*Micropterus salmoides*) that are the focus of research on mercury bioaccumulation [photos by the South Florida Water Management District (SFWMD) and the Florida Fish and Wildlife Conservation Commission (FWC)].

AMERICAN ALLIGATOR

The first report of total mercury (THg) in wild-caught American alligators (*Alligator mississippiensis*) from Florida waters was made by Ogden et al. (1974), who reported on levels in eggs collected from Shark River Slough in the ENP (the southern end of the EPA). They found concentrations of THg in alligator eggs greatly exceeded levels observed in the eggs of their estuarine counterpart, the American crocodile (*Crocodylus acutus*), collected from Florida Bay.

Measurements of THg in tail muscle from wild-caught alligators from Florida waters were first reported by Delany et al. (1988). They found that average concentrations in 32 alligators collected from eight lakes in 1984 ranged from 0.04 to 0.61 ppm. In 1989, responding to findings of elevated levels of THg in fish, the Florida Fish and Wildlife Conservation Commission (FWC) collected 29 harvestable-size alligators from the WCAs and tested for THg in tail muscle (**Table 3B-1**). THg levels were well in excess of previous findings from non-Everglades water bodies, with a system-wide range in individual alligators of 0.46 to 3.88 ppm and an average concentration of 2.38 ppm (Hord et al., 1990).

During the same time period, the FWC obtained samples of tail muscle (n = 19) collected by a nuisance-alligator hunter from alligators captured in urban canals on the eastern boundary of WCAs 2 and 3 in the Fort Lauderdale area. For comparison, an additional 58 samples of tail muscle were collected from licensed meat processors from north, central, and South Florida (Hord et al., 1990). Results for nuisance alligators from the Fort Lauderdale area during May 1989 revealed a wide range of values — individual concentrations ranged from 0.17 to 2.52 ppm with an overall mean of 0.74 ppm. The lack of precise location data for sample harvesting and the close proximity to the WCAs with their relatively high fish mercury concentrations were likely responsible for the highly variable THg concentrations in alligators. The results for alligators collected from meat processors from north, central, and South Florida (non-WCA locations) revealed lower THg concentrations with a range in county means of 0.13 to 0.90 ppm. The highest county mean, 0.90 ppm (n = 1), was from Franklin County in the panhandle, indicating that problematic levels of THg were not limited to the WCAs.

Table 3B-1. Range of total mercury (THg) concentrations in tail muscle from American alligators collected from Water Conservation Areas 2 and 3 (WCA-2 and WCA-3) by the FWC during two sampling events on February 2 and June 7, 1989 (adapted from Hord et al., 1990).

Canal Site	N	THg (ppm) Average (± SD)	THg (ppm) Min	THg (ppm) Max
C123	5	2.68 (0.82)	1.60	3.50
L35B	7	2.52 (0.82)	1.23	3.88
L38E	2	0.73 (0.38)	0.46	1.00
L67A	8	2.29 (0.72)	1.50	3.20
Miami	7	2.70 (0.97)	0.78	3.58
Both WCAs	**29**	**2.38**	**0.46**	**3.88**

N – number of alligators collected
SD – standard deviation
ppm – parts per million or milligrams per kilogram (mg/kg)

Further validation of the differences in bioaccumulation rates between the Everglades and the rest of the state came during a September 1989 survey of THg in alligator tail muscle conducted by the FWC. The average concentration of THg in 60 tissue samples collected from 12 peninsular lakes was 0.43 ppm (range, 0.05–1.40 ppm) (FWC, unpublished data). Testing of five randomly selected individuals of various sizes revealed that nearly all of the mercury (91 percent) in alligator tail muscle was methylmercury (MeHg), a highly toxic form of the element.

Results from these initial surveys clearly demonstrated that mercury was a state-wide water quality problem, with particular significance in the Everglades where bioaccumulation of mercury could have long-term ecological and human health impacts. The FWC had initiated a recreational alligator harvest in the Francis S. Taylor WMA in 1988; however, the finding of elevated levels of THg in wild alligators from the Everglades resulted in the closure of the 1989 and 1990 recreational alligator harvest in WCAs 2 and 3 based on Florida Department of Health and Rehabilitative Services' [now the Florida Department of Health (FDOH)] human consumption criteria. The criteria were that where mercury levels in fish or wildlife exceeded 1.5 ppm, the fish or wildlife should not be consumed by any segment of the population, while fish or wildlife with mercury levels exceeding 0.5 ppm should only be consumed in limited quantities. Based on those criteria and the mercury data, alligators from Francis S. Taylor WMA were placed in the "do not eat" category.

When open, the recreational alligator harvest quota for the Francis S. Taylor WMA was about 585 alligators per year, with a total economic loss of $27,000 during each year of closed harvest (Hord et al., 1990). The FWC re-opened the recreational harvest of alligators from the area in 2000. However, all specimens harvested were marked with a special color-coded tag identifying the alligator as taken from a mercury-contaminated area, and that the harvested meat could not be sold. Furthermore, it was highly recommended that the meat not be consumed by the hunter or anyone else. These protocols remained in effect at the time of this report.

Additional alligator tissue sampling was conducted by the FWC during the 1996 state-wide alligator harvest within 23 Alligator Management Units (AMUs) to define the spatial and temporal gradients in THg concentrations. Results again confirmed elevated levels of mercury in alligators collected from the WCAs (**Table 3B-2**). Within each AMU, between 10 and 12 individual tail muscle samples were composited for analyses of THg. Concentrations from 22 non-WCA AMUs ranged between 0.05 and 0.75 ppm (mean: 0.28 ppm), while the two composites from WCA-3A had concentrations of 1.62 and 1.90 ppm, respectively.

Table 3B-2. Range of THg concentrations in parts per million (ppm) in composite samples of American alligator tail muscle collected from select Alligator Management Units (AMUs) in 1996.

AMU	Location	Number in Composite	Composite THg (ppm)	Average Carcass Length (feet)	Range Carcass Length (feet)	Female	Male
104	Lake Hatchineha	12	0.34	6' 5"	4'2"-11'3"	5	7
107	Kiss. R. Pool B	12	0.67	7' 10"	6'4"-11'1"	3	9
201	St. Johns R. N.	11	0.19	6' 10"	5'0"-10'2"	11	
501	St. Johns R. 1	12	0.20	5' 9"	4'5"-7'11"	7	5
502	St. Johns R. 2	11	0.23	6' 5"	5'0"-8'9"	3	8
504	St. Johns R. 4	12	0.30	6' 1"	5'3"-8'3"	5	7
505	Lake Harney	11	0.30	7' 1"	4'11"-11'2"	2	9
508	Crescent Lake	12	0.15	5' 2"	4'1"-6'6"	7	5
509	Lake Griffin	10	0.15	9' 6"	8'0"-12'9"	4	6
511	Lake Harris	12	0.17	9' 11"	8'7"-12'0"		12
513	Lake Eustis	12	0.13	7' 7"	6'1"-9'3"	4	8
518	Lake Rousseau	12	0.27	6' 9"	4'3"-10'3"	5	7
601	Okeechobee W.	12	0.23	6' 3"	5'4"-7'3"	6	6
602	Okeechobee N.	10	0.20	8' 1"	6'8"-9'7"	1	9
711	Lake Hancock	12	0.05	8' 5"	6'3"-13'2"	6	6
722	Orange Lake	12	0.38	8' 10"	5'4"-11'1"	2	10
734	Lake Seminole	10	0.29	7' 8"	4'1"-11'7"	5	5
741	Lake Trafford	10	0.63	7' 11"	6'2"-10'4"	4	6
751	Lake George	10	0.14	7' 10"	5'11"-9'6"	3	7
110	Lake Kissimmee	11	0.75	8' 7"	6'3"-12'10"	1	10
515	L. Panasoffkee	12	0.13	4' 11"	4'2"-6'2"	6	6
517	Withlacoochee S.	12	0.31	5' 6"	4'1"-7'8"	8	4
	Non-Water Conservation Area (WCA) Average		**0.28**				
403	WCA-3A North	11	1.62	5' 3"	4'1"-6'4"	4	7
401	WCA-3A South	11	1.90	6' 4"	4'0"-9.6"	4	7
	WCA Average		**1.76**				

Similarly, Heaton-Jones et al. (1997) reported that THg concentrations in various tissues from alligators collected during 1992–1993 from non-Everglades locations in Florida varied widely with geographic origin but were between those collected from alligator farms (low THg concentrations) and the WCAs (high concentrations). Alligators collected from the Everglades (in WCA-2 and WCA-3), were significantly higher in THg than farm-raised animals for a number of tissues, including tail muscle. Mean THg concentrations in farm-raised, non-WCA, and WCA alligators were 0.10 ± 0.06 ppm, 0.33 ± 0.28 ppm, and 2.61 ± 0.91 ppm, respectively. During this study, an alligator size-dependence in THg bioaccumulation was noted; however, other datasets have been inconsistent in demonstrating increased THg concentration with alligator size. The levels of THg found in WCA alligators were not unprecedented; Yanochko et al. (1997) found similar levels in other mercury-enriched locations in the southeastern United States.

Concentrations of THg in alligator muscle collected through the 1990s clearly demonstrated THg levels exceeding the existing criteria established for the protection of human health by the FDOH and U.S. Environmental Protection Agency (USEPA, 2001a). The USEPA human health criterion for fish consumption for MeHg of 0.3 ppm was exceeded by all WCA alligators and also by alligators from several AMUs sampled during the mid-1990s.

Although many fish from the WCAs continue to exceed the USEPA human health fish tissue MeHg criterion, recent declines have been evident (Gabriel et al., 2010b). It is not known if concurrent declines in alligator mercury levels have occurred because samples have not been collected from the WCAs since 1996.

The FWC is interested in conducting a human health risk assessment to determine the viability of allowing sale and consumption of meat from recreationally caught alligators from the WCAs. Alligator sampling in several areas adjacent to the WCAs has occurred in recent years. In consideration of establishing alligator hunts in several Stormwater Treatment Areas (STAs), collections of 12 harvestable size alligators were made from both Stormwater Treatment Area I West (STA-1W) and Stormwater Treatment Area 5 (STA-5) in 2008, and from Stormwater Treatment Area 3/4 (STA-3/4) in 2010 by the FWC and the SFWMD. THg concentrations in STA alligators were much lower than previous findings from the adjacent WCAs, with average concentrations less than the USEPA MeHg criterion for human consumption. Average concentrations of 0.084 ppm (0.032 to 0.266 ppm), 0.113 ppm (0.048 to 0.329 ppm), and 0.277 ppm (0.110 to 0.771 ppm), and were observed in STA-1W, STA-5, and STA-3/4, respectively.

Whether these results include data from alligators that move in and out of the adjacent WCAs is unknown; the STAs typically have fish populations with significantly lower THg levels than the WCAs (Gabriel et al., 2010c). In 2010, 12 alligators were harvested from the Holey Land Wildlife Management Area (Holey Land WMA) when establishment of a hunt on the property was being considered. Long-term monitoring of fish from the Holey Land WMA has revealed increasing concentrations in THg during the past decade with only recent declines (Axelrad et al., 2009; Gabriel et al., 2010a). Not unexpectedly, THg levels in alligators were elevated with an average concentration of 1.16 ppm (range: 0.54–2.56 ppm). Again, there is the potential for alligators to forage within the adjacent wetlands of WCA-3 and STA-3/4. Current mercury levels in the WCAs are unknown.

The FWC and the FDEP plan to reassess the need for the human health protection guidance presently in place for the WCA-2 and WCA-3 recreational alligator harvest by collecting and analyzing up to 200 alligators (150 from the Francis S. Taylor WMA AMU and 50 from other state-wide AMUs) during the 2011 state-wide recreational alligator harvest. Results are expected to be used for human health risk assessments specifically for each AMU.

FLORIDA PANTHER

The Florida panther (*Puma concolor coryi*) is a state and federally listed endangered species. Environmental stressors (including environmental contaminants), low genetic variability, and habitat loss have all contributed to the decline of this species. Mercury contamination has been suggested as a causative factor in the low densities, poor reproduction, and some reported deaths of panthers from portions of South Florida (Roelke et al., 1991; Facemire et al., 1995); however, factors such as prey abundance and consumption, panther diseases, genetics, and demographic issues are difficult to separate from the influence of mercury when measuring panther fitness and mortality. During a survey of various tissue, blood, and hair samples collected from 52 live and dead free-ranging panthers from 1978–1991, Roelke et al. (1991) found detectable levels of THg in all tissues as well as strong spatial gradients. Similarly, MeHg was present in all panther hair samples collected from museum specimens dating back to the 1890s (Newman et al., 2004), with significantly higher levels observed in the 1990s than in the late 1800s.

Roelke et al. (1991) reported that the highest mercury concentrations were found in panthers from the Shark River Slough of the ENP (hair = 56.4 ppm; blood = 0.794 ppm) and the lowest concentrations were from north of Alligator Alley (hair = 1.66 ppm; blood = 0.094 ppm), which included northern Fakahatchee Strand, Florida Panther National Wildlife Refuge (FPNWR), and portions of Big Cypress National Preserve (BCNP). Differences were likely influenced by the ambient levels of mercury in the environment as well as prey selection, with panthers feeding on non-hoofed, fish-eating species [i.e., raccoons (*Procyon lotor*)] exhibiting the highest tissue THg concentrations. [Note: Animal tissue (fish, panther, etc.) are usually reported as mg/kg (ppm); blood is mg/L (ppm).]

It was noted that raccoons comprised 70 percent or more of the diet of panthers foraging within Shark River Slough. These panthers also had the highest muscle and liver THg concentrations. Panthers foraging north of Alligator Alley had lower mercury levels and fed primarily on white-tailed deer (*Odocoileus virginianus*) and feral hogs (*Sus scrofa*) — species not tied to the aquatic food web. During the late 1980s, adaptive management strategies by the FWC to modify the prey base available to panthers foraging within the Fakahatchee Strand resulted in declines in panther THg levels, as panthers transitioned from a diet dominated by raccoons to one comprised largely of deer and hogs (Roelke et al., 1991). At that time, raccoons within Fakahatchee Strand had THg values 10–100 times higher than those in deer.

More recently, declines in THg levels in Everglades fish (Lange et al., 2000, 2005; Gabriel et al., 2010a), birds (Rumbold et al., 2001; Frederick et al., 2002), and alligators from certain regions of the Everglades (Rumbold et al., 2002) have been reported. This led Barron et al. (2004) to conclude that current risks to panthers from mercury exposure are low. Based on a dietary exposure model, pre-1992 levels of mercury in panther prey suggested a 46 percent probability of exceeding chronic dietary thresholds for MeHg. Based on an estimated 70–90 percent decline in mercury exposure to panthers during the subsequent decade, panthers in 2002 faced a less than 4 percent probability of exceeding dietary thresholds. Barron et al. (2004) further concluded that under a worst-case scenario, panthers consuming raccoons only faced a 4.5 percent risk of developing clinical symptoms of mercury exposure that could lead to death. However, there is evidence that mercury hot spots in the Everglades continue to exist or could develop in response to restoration activities, increasing risks to panthers through dietary exposure.

From 2000–2007, the FWC gathered a total of 272 blood samples and 384 hair samples from panthers for mercury analysis. Preliminary results for these collections were reported by Brandon et al. (2009). Blood samples (n = 158) had measurable amounts of mercury, with concentrations ranging from 0.009 ppm to 5.3 ppm. Likewise, hair samples (n = 321) also had measurable concentrations of mercury, with values ranging from 0.086 ppm to 100 ppm. During this period, the panther with the highest mercury concentrations in blood and hair (from samples collected post-mortem), identified as FP 85, was first caught in the Southern Glades Wildlife Management Area in 2003 and then found dead in the ENP in 2004. The cause of death for FP 85 was listed as "unknown" (FWC, 2010).

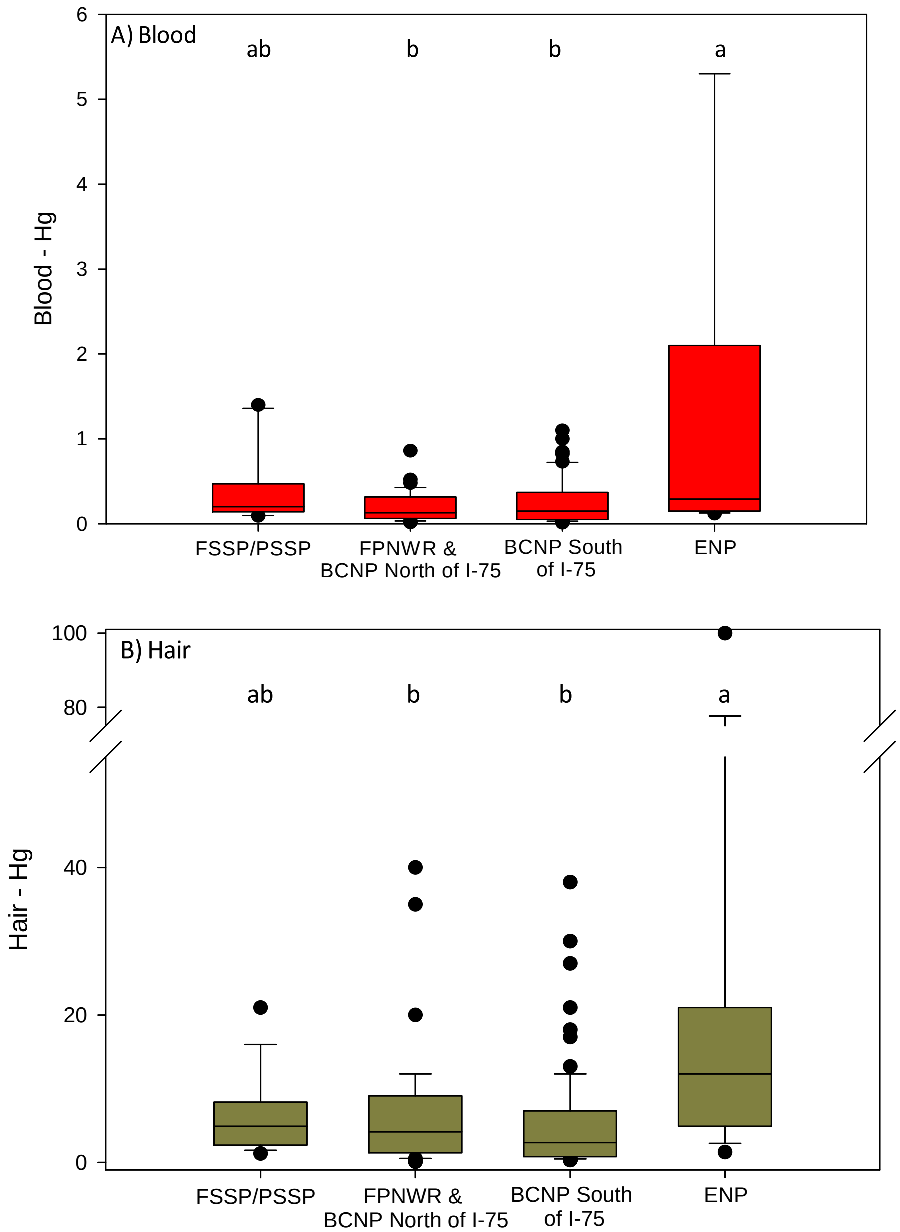
Average mercury concentrations in the hair and blood of Florida panthers has decreased in most geographic regions (Roelke et al., 1991) with the possible exception of areas north of I-75, including north BCNP and the FPNWR, where concentrations have remained relatively unchanged (**Table 3B-3**). Spatial gradients in the panther mercury levels persisted for the 2000–2007 period, with the highest mean concentrations in hair and blood of the four regions originally identified by Roelke et al. (1991) found in the ENP (**Figure 3B-2**). Differences among these regions were statistically significant as indicated in **Figure 3B-2** in blood (Kruskal-Wallis One Way Analysis of Variance on Ranks, h = 13.541, df = 3, p = 0.004; Dunn's Method for pairwise multiple comparison p = < 0.05) and in hair (h = 16.765, df = 3, p = < 0.001; Dunn's Method for pairwise multiple comparison p = < 0.05). Roelke et al. (1991) suggested that panthers inhabiting areas with less dense ungulate populations, like the ENP, may rely more heavily on fish-eating wildlife, such as raccoon and alligators, thereby increasing their potential for mercury accumulation through trophic transfer.

Table 3B-3. Variation in blood Hg and hair Hg (ppm) between periods of intensive sampling among geographic regions. Data from 1978–1991 and geographic regions from Roelke et al. (1991), table adapted from Brandon et al. (2009).

	Florida Panther Mercury Levels					
	1978–1991			2000–2007		
Assay (ppm)	N	Mean	SE	N	Mean	SE
Florida Panther National Wildlife Refuge & Big Cypress National Preserve, North of I-75						
Blood	42	0.1	1.15	38	0.13	0.03
Hair	43	1.66	1.23	48	3.26	1.13
Fakahatchee & Picayune						
Blood	12	0.38	1.35	11	0.25	0.14
Hair	7	7.18	1.62	14	4.46	1.39
Big Cypress National Preserve, South of I-75						
Blood	2	0.62	1.26	50	0.14	0.04
Hair	2	42.3	1.63	90	2.65	0.75
Everglades National Park & East Everglades*						
Blood	7 & 14	0.23–0.79	1.2–1.6	15	0.57	0.46
Hair	8 & 8	10.9–56.4	1.24–1.35	17	11	6.4

N – northern
SE – southeastern

*Note: Roelke et al. (1991) subdivided this region into two smaller areas, which could not be duplicated with any certainty for this assessment. Animal tissue (fish, panther, etc.) are generally reported as mg/kg (ppm); blood is mg/L (ppm).



Note: Box plots represent the median, 25th and 75th percentiles; whiskers the 10th and 90th; points are outliers. Sites with similar letter designations (e.g., a and ab) did not differ significantly. Sites from Roelke et al. (1991) include Fakahatchee and Picayune State Parks (FSSP & PSSP), Florida Panther National Wildlife Refuge (FPNWR), Big Cypress National Preserve (BCNP), and Everglades National Park (ENP) (figure from Brandon et al., 2009).

Figure 3B-2. Geographical variations in (A) blood Hg and (B) hair Hg (ppm) from 52 free-ranging Florida panthers collected 2000–2007.

Although average mercury concentrations in Florida panther blood and hair generally declined between study periods (1978−1991 and 2000−2007) at Big Cypress National Preserve (BCNP) south of I-75, increasing mercury levels in blood and hair were observed in recent years (**Figure 3B-3**). Mean concentration of mercury in blood rose from 0.259 ppm (n = 6) in 2006 to 0.568 ppm (n = 8) in 2007 and more than doubled in hair from 4.518 ppm in 2006 (n = 9) to 10.847 ppm (n = 13) in 2007. This difference between years was not statistically significant for blood or hair, but because of the few animals left in the wild, any data indicating elevated panther mercury levels are cause for concern.

It appears that maximal mercury concentrations in panthers were evident in the late 1980s and early 1990s, with subsequent declines across much of the Everglades landscape. The possible recent increase in mercury levels in panthers from certain areas, especially the Big Cypress region (BCNP), is cause for concern due to the concentration of animals inhabiting this area. Because the Florida panther is an endangered species, mercury exposure levels remain a concern.

It is evident that the majority of the current Florida panther population occupies an area where mercury bioaccumulation in aquatic ecosystems remains a significant concern. The FWC continues to collect blood and hair samples for mercury analysis. Current efforts focus on filling the data gap from 1992 through 1999, and on more in-depth analysis of existing data, including the 1978–1991 and 2000–2007 datasets. Analyses will focus on developing a better understanding of potential influential variables contributing to mercury exposure (such as panther age and sex, and regional hydrology). Moreover, correlation analyses of mercury levels with health metrics such as body condition, blood chemistry, and reproductive success should be conducted on the expanding dataset and compared to literature-derived critical tissue concentrations to elucidate the direct and indirect effects of mercury on individuals and regional sub-populations. Finally, special consideration should be given to regional and individual maximum exposure levels observed in panthers due to their endangered status.

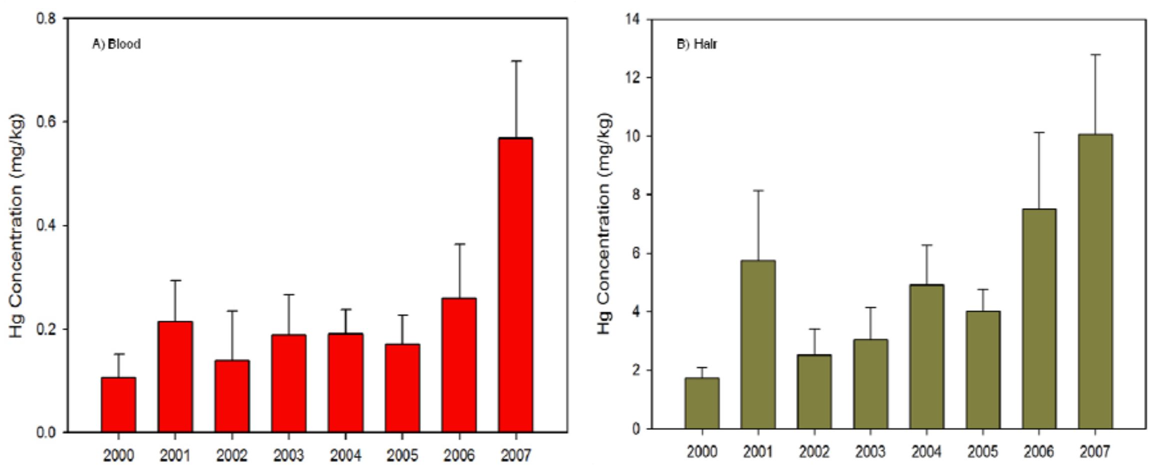


Figure 3B-3. Temporal variation in mercury concentrations [mean ± 1 standard deviation (SD), mg/L = ppm for blood; mg/kg = ppm for hair] in (A) blood and (B) hair of Florida panthers collected from 2000−2007 in Big Cypress National Preserve (BCNP), south of I-75 (figure from Brandon et al., 2009).

BURMESE PYTHON

The Burmese python (*Python molurus bivittatus*) is native to Southeast Asia and has been exported to the United States for the pet trade and ultimately released into the wild. These snakes thrive in the subtropical South Florida climate. Other species of pythons have been found in Florida, but the Burmese python is the only species that has been confirmed to breed in the wild (Harvey et al., 2008). Due to increases in their populations, state and federal agencies are working to control pythons. The Burmese python is a priority invasive species under the Research Coordination Verification and Assessment program of the Comprehensive Everglades Restoration Plan (see Chapters 6 and 9 of this volume). In January 2008, the FWC established a list of Reptiles of Concern (ROC) for nonnative species which includes pythons. In July 2009, a permit program was initiated to allow hunting of ROCs in FWC-managed areas. There is concern, however, that hunters may consume the python meat, which has high concentrations of mercury.

Mercury data were collected from 24 Burmese pythons in the ENP from 2006–2009 by the U.S. Geological Survey (Krabbenhoft, unpublished data). The mean THg concentration in muscle tissue of 3.6 ppm (range: 0.14–10.75 ppm) was significantly higher than in fish and alligators within the ENP (**Figure 3B-4**) and showed no relationship to python size. Most of the mercury burden in pythons appears to be in the methylated form, with an average MeHg fraction of 80 percent in 11 co-sampled individuals (range: 67–96 percent). Analysis of the digestive tracts of captured pythons in Florida show some of the species consumed are raccoons, wading birds, and alligators (Snow et al., in press), which could account for the high concentrations of mercury since all of these species are fish-eating. Continued monitoring of mercury in captured pythons is planned by the National Park Service (NPS) and FWC.

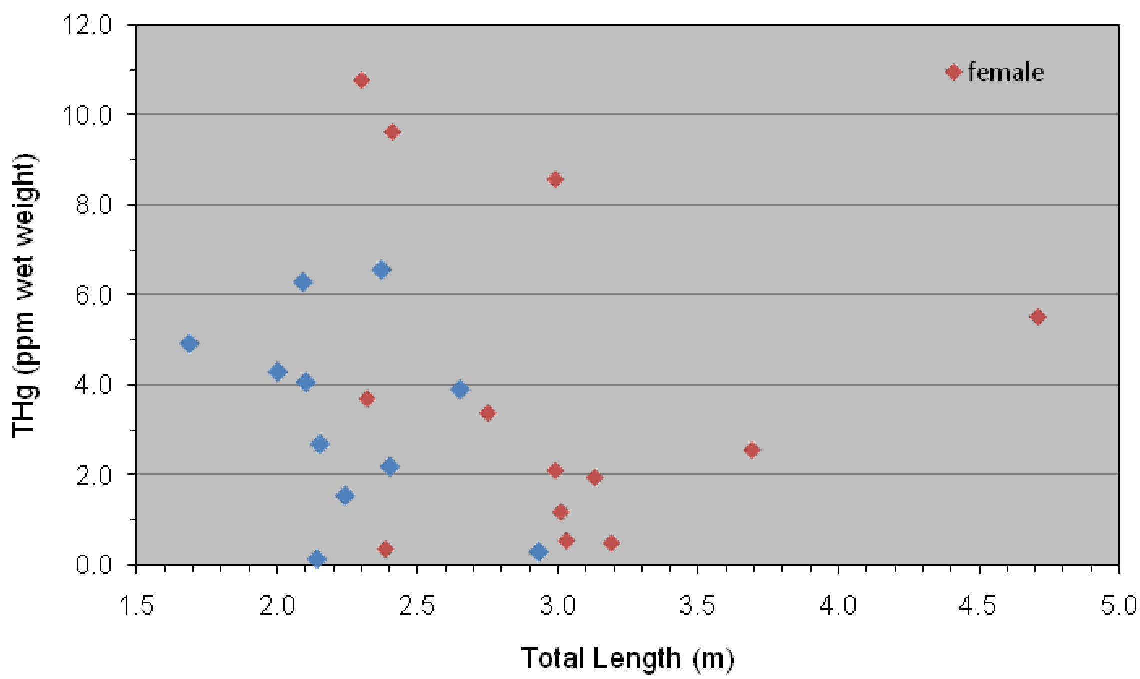


Figure 3B-4. Mercury concentrations (ppm) with size (total length) in Burmese pythons collected in Everglades National Park (ENP or Park) from 2006–2009 (figure from D. Krabbenhoft, U.S. Geological Survey, personal communication).

FISH IN THE EVERGLADES PROTECTION AREA

Largemouth bass (LMB) (*Micropterus salmoides*) were collected from the EPA and other South Florida sites during the current-year sampling period from July 2009 through June 2010 using direct-current electro-fishing equipment (**Figure 3B-5**). The same methods were used to collect LMB from downstream receiving waters of the EPA and STAs and are reported in Appendices 3B-1 and 5-5 of this volume, respectively.

In the laboratory, LMB were weighed, measured, sexed, and the sagittal otoliths were removed for determination of age as described by Taubert and Tranquilli (1982). An entire skinless axial muscle fillet was homogenized and an aliquot submitted to the FDEP Central Laboratory in Tallahassee where THg determinations were made using USEPA Method 245.6 (Mercury in Tissues by Cold Vapor AAS). The minimum detection limit (MDL) was 0.02 ppm.

A subset of samples was analyzed by the SFWMD using USEPA Method 7473 (Mercury in Solids and Solutions by Thermal Decomposition, Amalgamation, and Atomic Absorption Spectrophotometry). The MDL was 0.005 ppm. A portion of the samples were analyzed by both methods and evaluated to determine comparability. All results are reported as THg on a wet-weight basis as micrograms per gram (µg/g) (1 µg/g = 1 ppm). Because more than 85 percent of the mercury found in top-level predatory fish such as LMB is in the form of MeHg (Grieb et al., 1990; Bloom, 1992). The assumption is made that THg is equal to MeHg concentration in LMB samples.

Figure 3B-5. Fish collections within the Everglades Protection Area (EPA) typically are conducted in open marsh, along airboat trails, and in canals using direct-current electro-fishing equipment mounted either on an airboat or jon boat (photos by the FWC).

Monitoring of mercury in LMB tissue from the Everglades integrates spatial and temporal exposure to MeHg. This is particularly relevant where LMB can move over large areas in response to changes in hydroperiod, with prey selection varying between habitats (i.e., canal or marsh). Mercury levels in LMB are also reflective of variations in fish size and age, population turnover, trophic position, and trophic exchange rates. Using relatively long-lived LMB as a monitoring tool is a distinct advantage because these fish accumulate high concentrations of mercury over their life span, thus allowing detection of concentration gradients within their feeding ranges. LMB are also readily available throughout the Everglades, have well understood feeding ecology and life histories, and are directly relevant to public health policy.

To eliminate redundancy, regional trends in LMB THg concentrations are reported and site-specific trends are referenced when necessary from Appendices 3B-1 and 5-6 of this volume. The only exception is that trends from the Holey Land WMA, represented by only one site, are reported in this chapter (see Appendix 3B-1).

From July 2009 through June 2010, 183 LMB were collected from the WCAs, 40 were collected from Shark River Slough in the ENP, 20 were collected from Holey Land WMA, 20 from STA site, STA1WC3, and 40 from the Kissimmee Chain of Lakes (KCOL). Data for 5,281 LMB collected from 1989–2010 are summarized by region to compare and contrast trends in mercury concentrations within the EPA, STA-1W, and the Northern Everglades (represented by the KCOL). Single-year data (2009–2010 sampling period) are briefly summarized in the *Fish in the Greater Everglades* section of this chapter and in Appendix 3B-1 of this volume.

Comparisons were made among five regions, from south to north, including Shark River Slough in the ENP (SHARK region); WCA-1, WCA-2, and WCA-3 within the EPA (WCA region); STA-1W, Cell 3 (STA1W region); Holey Land Wildlife Management Area (HOLEY region); and from the Northern Everglades, three lakes within the KCOL, including Lakes Kissimmee, Tohopekaliga, and East Tohopekaliga (KISS region) (**Table 3B-4**). Site locations for long-term monitoring sites are presented in **Figure 3B-6**.

Table 3B-4. Description and period of record (POR) for fish collection sites within each region. Sampling events typically represent one collection each year per region, but may vary.

Region	Site Names	Description	Site POR	Sampling Events	# LMB
Stormwater Treatment Area 1 West (STA-1W)	ENR012	Both sites located within Cell 3 of STA1W	1995–2009	15	492
	ENR302		1995–2009		
Holey Land WMA	HOLEY (in the north borrow canal)	Holey Land Wildlife Management Area	1990–2009	15	284
Shark River Slough	ENPNP	Both sites are within Shark River Slough in ENP	1993–2010	19	529
	L67X		1989–2009		
Water Conservation Areas	WCA-1	11 canal and marsh long-term monitoring and 42 random sites within WCAs 1, 2, and 3	1989–2009	21	3,173
	WCA-2		1989–2009		
	WCA-3		1989–2009		
Northern Everglades [Kissimmee Chain of Lakes (KCOL)]	LK Kissimmee	Lake samples	1989–2006	21	803
	LK Tohopekaliga		1989–2010		
	E. LK Tohopekaliga		1989–2010		

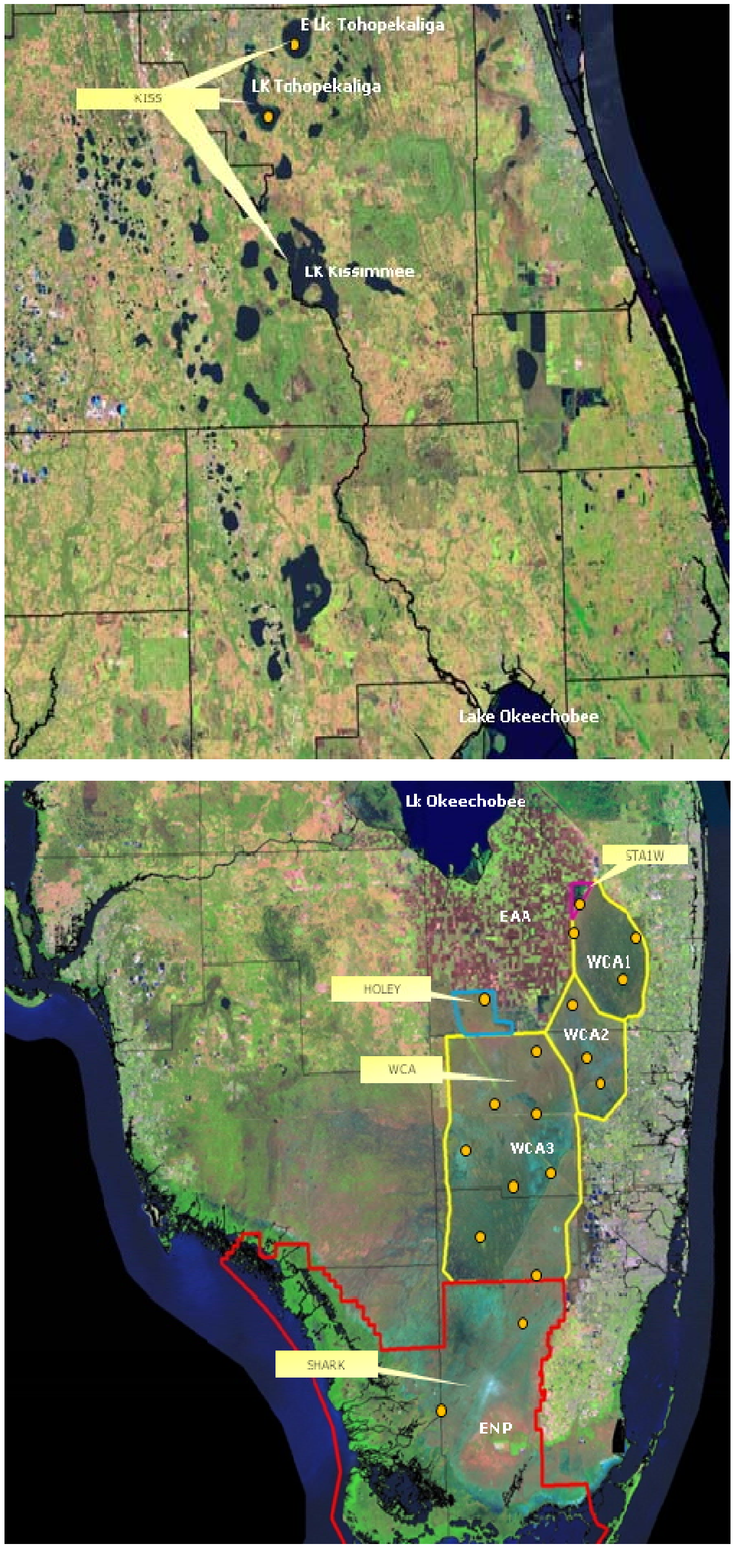


Figure 3B-6. Regional boundaries for annual LMB median THg concentrations indicating location of long-term monitoring sites (●) for region KISS in the Northern Everglades (top) and regions STA-1W, HOLEY, WCA, and SHARK in the Southern Everglades (bottom). [Note: Less frequently sampled locations are not shown.]

Regional LMB THg concentrations were normalized to a standard fish length in this year's report. Because THg concentrations in LMB vary with size and age (Wiener et al., 2006; Lange et al., 1994) and because size distributions, sex, and collection date vary among sites, THg concentrations in individual LMB were normalized by dividing the THg value by fish total length (TL) in millimeters (mm). Moreover, in order to relate the resultant concentration to a human health end-point, the value (ppm/mm) was multiplied by 356 mm (14″) to represent the upper range of the legal LMB size range available for harvest by anglers. In the Everglades region, anglers are allowed to harvest up to five LMB up to 14″ TL as well as one fish exceeding 14″ per day; however, most LMB exceeding 14″ are voluntarily live-released.

For previous SFERs, normalization of mercury concentrations by fish age proved to be a successful method to assess spatial and temporal distributions of LMB THg concentrations in Florida (Lange et al., 1993 and 1994; Gabriel et al., 2010b), because this reduced the influence of sexually dimorphic growth on mercury bioaccumulation rates between male and female LMB (Lange et al., 1994). Normalization by regressing mercury with age is desirable when assessing trends among individual sites, but TL data were both more readily available and better for assessing trends. Using TL enables use of all available data to assess trends across multiple sites within a region where age-standardization would not provide a link to size-specific human health criteria. While annual medians for TL normalized data were highly correlated with non-normalized data (**Figure 3B-7**), TL normalized data provide a link to a measurable human health end-point and better describe differences in THg concentrations among regions.

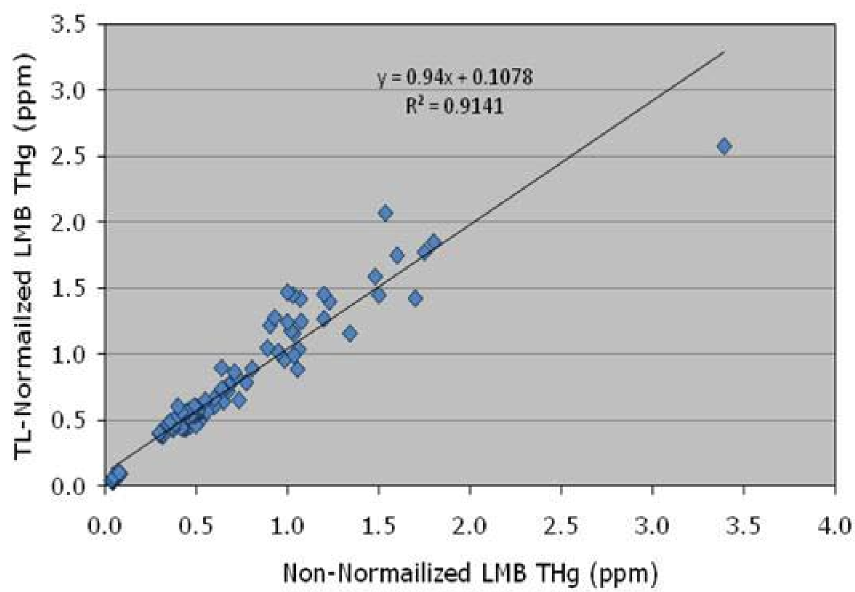


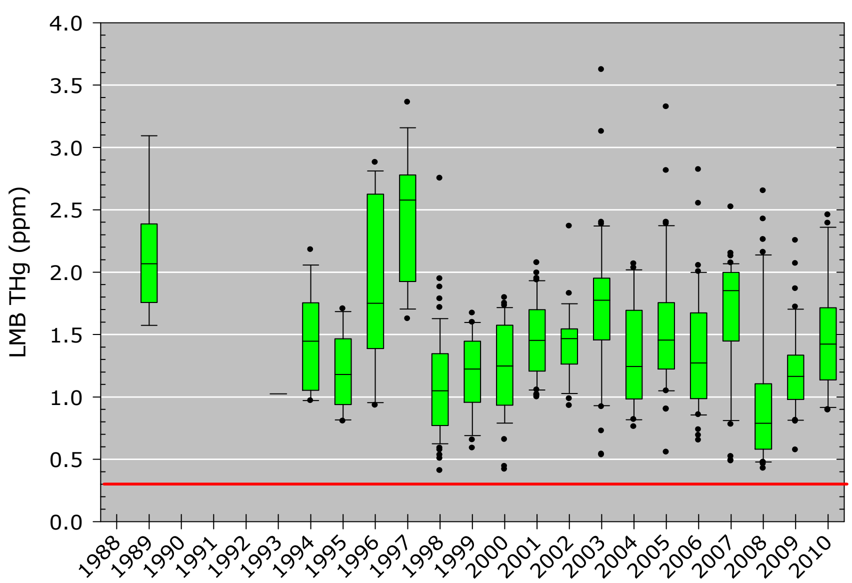
Figure 3B-7. Relationship between annual regional median non-normalized and normalized THg concentrations for largemouth bass (LMB) (*Micropterus salmoides*) collected during sampling events from 1989–2010.

LMB have been collected for mercury analyses from two sites, L67F1 and ENPNP in Shark River Slough almost yearly since 1989 (**Figure 3B-8**). Regional medians in the slough remain elevated over other areas within the EPA, making Shark River Slough a significant mercury hot spot; levels continue to exceed the 0.3 ppm USEPA MeHg criterion for the protection of human health. The median THg concentration peaked in 1997 at 2.58 ppm (range; 1.63–3.36 ppm; n = 14) and was 1.43 ppm (range; 0.89–2.46 ppm; n = 20) in 2010; however, the 2010 median represents a short-term (two-year) increase of 80 percent from a median of 0.79 ppm in 2008. Although annual median LMB mercury concentrations have varied over the short term in Shark

River Slough, seasonal Kendall analysis found no significant (r = -0.018; p = 0.9164) trends over the entire period of record (POR) indicating continued conditions favorable to MeHg production and bioaccumulation.

Similarly, across the EPA, near maximal cumulative mean THg concentrations in mosquitofish (*Gambusia holbrooki*), sunfish (*Lepomis* spp.), and LMB have been found at site L67F1 in the upper reaches of Shark River Slough (see Appendix 3B-1 of this volume). Maximal mosquitofish THg concentrations occurred in central Shark River Slough during wet seasons in 1995 and 2005 (USEPA, 2001b; Scheidt and Kalla, 2007). In contrast, aqueous MeHg concentrations in Shark River Slough tend to be lower than most other areas of the EPA (USEPA, 2001b; Scheidt and Kalla, 2007). While across much of the EPA, mercury levels in epiphytic periphyton were strongly related to mercury uptake in mosquitofish, in a core area of Shark River Slough, a strong relationship was found between aqueous MeHg and uptake in mosquitofish (Kalla et al., 2008) suggesting a mechanism for the high bioaccumulation factors in this area (USEPA, 2001b).

Within the wetlands of Shark River Slough, dissolved organic carbon (DOC) concentrations are variable in response to dry/rewet cycles (Scheidt and Kalla, 2007); however, DOC levels are generally low compared with the rest of the EPA. Dry/rewet cycles, common seasonally in the region, have been demonstrated to temporarily increase production of sulfate (Orem et al., 2008) and release labile carbon and sediment-bound inorganic mercury (Krabbenhoft and Fink, 2001) to stimulate MeHg production. Wet season deposition of inorganic mercury would additionally increase substrate for MeHg production and perhaps provide the seasonal pulses of bioavailable MeHg necessary to drive short-term variations in LMB THg concentrations. Although LMB integrate MeHg over a protracted period of time [LMB here normalized to TL = 14″ (356 mm), mostly age class 2 and 3 in the ENP], pulses of aqueous MeHg have been shown to move quickly (< 1 yr) through the food web into high trophic level fish (Krabbenhoft and Fink, 2001; Rumbold and Fink, 2006).



Box plots represent the median, 25th and 75th percentiles; whiskers the 10th and 90th percentile; and points are outliers. The 0.3 ppm U.S. Environmental Protection Agency (USEPA) methylmercury (MeHg) criterion is indicated in red.

Figure 3B-8. Annual summaries of mercury concentrations [normalized to total fish length = 356 millimeters (mm)] for LMB collected from sites L67F1 and ENPNP in Shark River Slough within the ENP from 1989–2010.

In addition to LMB, several other species of fish found within Shark River Slough exceeded the USEPA MeHg criterion for the protection of human health (USEPA, 2001a). The FDOH continues to issue no-consumption advisories for LMB, common snook (*Centropomus undecimalis*), spotted sunfish (*Lepomis punctatus*), and yellow bullhead (*Ameiurus natalis*). The FDOH further recommends limited consumption of redear sunfish (*L. microlophus*), bluegill (*L. macrochirus*), and the nonindigenous Mayan cichlid (*Cichlasoma urophthalmus*) from Shark River Slough waters (FDOH, 2009). Mercury bioaccumulation in Shark River Slough appears to be elevated over other areas of the ENP (Axelrad et al., 2009), but the entire Park is subject to advisories urging limited consumption of fish. The impacts of mercury on estuarine species in downstream reaches of Shark River Slough and into the Gulf of Mexico are uncertain because the processes affecting bioaccumulation of mercury are not well understood.

In the WCAs, a total of 3,173 LMB were collected from 53 sites over the POR (1989–2009) (see **Table 3B-4**). Long-term monitoring locations within the WCAs are shown in **Figure 3B-6**. Annual mercury medians in LMB have varied over the POR but have generally declined from a maximum of 1.59 ppm in 1991 to a minimum of 0.40 ppm in 2001, representing a 75 percent decline (**Figure 3B-9**). By 1998, median concentrations in LMB across the WCAs stabilized, and have varied little since then (range: 0.40–0.61 ppm). Over the entire POR, seasonal Kendall analyses indicate a significant ($r = -0.63810$; $p < 0.001$) decline in THg levels in LMB with an overall decline of 62 percent since 1991.

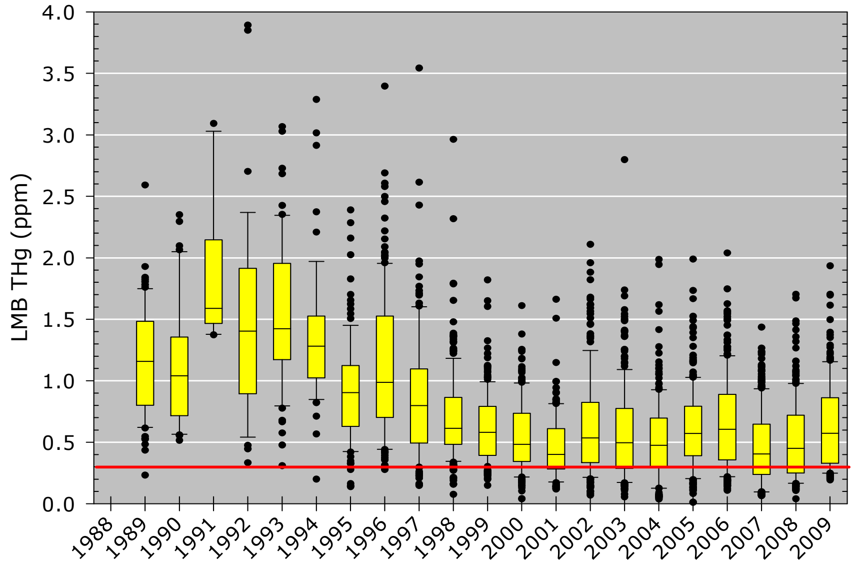
Based on extensive surveys in 1995 and 1996, the USEPA (1998) identified several hot spots where THg levels in mosquitofish were almost twofold higher than the Greater Everglades basinwide average. One of these MeHg hot spots, site CA315 within WCA-3A, received focused attention for a decade in order to better understand system controls on MeHg production and bioaccumulation.

Declines in sulfate concentrations in the WCAs during the late 1990s likely resulted in rapid declines in MeHg production and concomitant declines in fish THg concentrations (USEPA 2001b and 2007; Kalla et al., 2010; Krabbenhoft et. al, 2010). However, other factors affecting temporal and spatial patterns of MeHg production and THg bioaccumulation in fish are likely important in explaining the smaller variations in LMB mercury levels detected since 1998.

For example, spatial patterns of fish THg concentration within the WCAs have shifted as concentrations in fish representing three distinct trophic levels (mosquitofish, sunfish, and LMB) from site WCA2U3 (farther upstream) now exceed those from CA315 (see Appendix 3B-1 of this volume). In addition, within WCA-2, divergent trends in fish THg are evident. At site WCA2U3 (farther downstream), these three fish species have shown recent THg increases, while at the same time declines were observed for the same species at site CA2NF. These divergent trends occurred within WCA-2, but at sites with different nutrient inputs, hydrologic regimes, and food web structures. The influence of food web dynamics, water quality, sediment parameters, and hydrologic regimes on MeHg production and bioaccumulation are slowly being resolved (USEPA, 2007; Kalla et al., 2010; Krabbenhoft et al., 2010) to further elucidate their influence on MeHg production and bioaccumulation in fish.

Not only have median LMB THg concentrations declined as a whole across the WCAs, but the number of individual LMB exceeding 2 ppm decreased from 56 for POR 1988–2000 to only three for POR 2001–2009 (**Figure 3B-9**). The maximum LMB mercury concentration in individual, legally harvestable fish has decreased over time, ranging from 3.89 ppm (from canal site L67A in 1992) to 2.8 ppm (from canal site L35B in 2003). Nonetheless, median concentrations of mercury in LMB continue to exceed the USEPA human-health fish tissue criterion (USEPA, 2001). From 2001–2009, over 58 percent of all LMB (n = 1,306) exceeded that criterion in the WCAs (**Figure 3B-10**). The WCAs provide important fishing opportunities within the Francis S. Taylor WMA (WCA-2 and WCA-3) and within Arthur R. Marshall

Loxahatchee National Wildlife Refuge (which contains WCA-1) for both LMB and other sport fish. The FDOH has issued advisories for LMB and eight other species of fish, recommending limited or no consumption of fish caught from the WCAs (FDOH, 2009). Due to (1) continued high rates of atmospheric deposition of mercury, (2) the rich, organic soils, and (3) sulfate enrichment, mercury remains a water quality concern in the WCAs.



Notes: Box plots represent the median, 25th and 75th percentiles; whiskers the 10th and 90th; and points are outliers. The 0.3 ppm USEPA MeHg criterion is indicated in red.

Figure 3B-9. Annual pooled summaries of Hg concentrations (normalized to total fish length = 356 mm) in LMB collected from canal and marsh sites in WCA-1, WCA-2, and WCA-3 from 1989–2009.

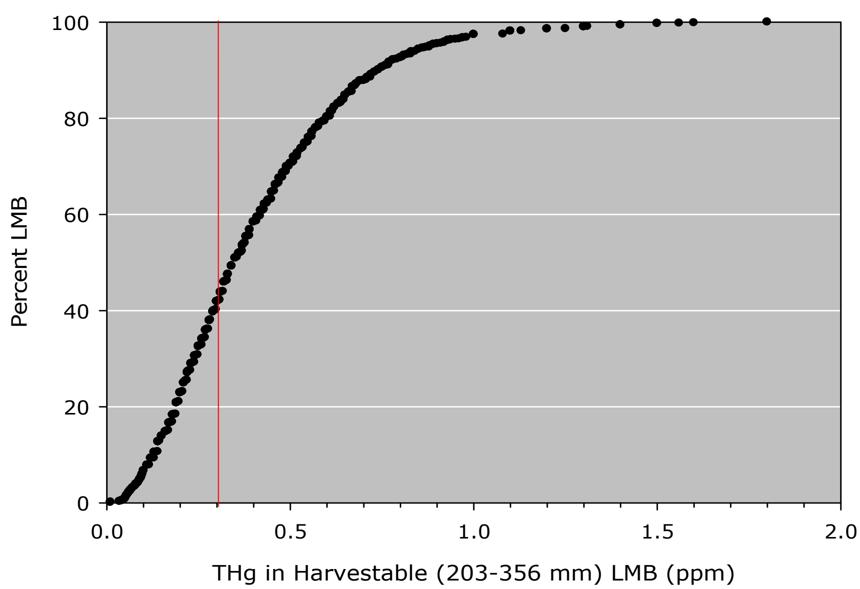


Figure 3B-10. Cumulative distribution of harvestable size LMB [203–356 millimeter (mm) length] collected from WCAs 1, 2, and 3 during 2001–2009. Fifty-eight percent of all LMB exceeded the USEPA human health criterion of 0.3 ppm (red line).

FISH IN THE GREATER EVERGLADES

LMB THg concentrations trends outside the EPA have been determined for sites in STA-1W (Cell 3), Holey Land WMA, and the KCOL (see **Figure 3B-6**). Sites in STA-1W and the Holey Land WMA are located interior to hydrologically managed wetlands adjacent to the WCAs, while the KCOL represent three long-term datasets from the Northern Everglades.

The two sample sites representing STA-1W (sites ENR003 and ENR012; see Gabriel et al., 2009 for site descriptions) were not significantly different in LMB THg concentrations when compared among years (paired t-test, $p > 0.05$); therefore, data were pooled to represent STA-1W, Cell 3. In general, LMB from the interior cells of STA-1W have had the lowest concentrations of THg among all of the STAs since inception. Of a total of 492 LMB collected for POR 1995–2009, only five exceeded the USEPA criteria for the protection of human health. Median THg concentrations varied little during the POR with annual medians ranging from 0.04–0.11 ppm and no trends evident (**Figure 3B-11**). There were concerns that the Everglades Nutrient Removal Project, the precursor to STA-1W, would promote high rates of mercury methylation and bioaccumulation due to inundation of organic-rich soils, suggested by previous studies of newly created reservoirs (Abernathy and Cumbie, 1977; Bodaly et al., 1984; Verdon et al., 1991). Ultimately, the man-made wetland functioned as a mercury sink, removing about 70 percent of the inflow mass (Miles and Fink, 1998; Rumbold and Fink, 2006).

In contrast, in 2000, Cell 1 in the newly constructed STA-2 exhibited anomalously high MeHg concentrations in fish and water soon after start-up (Rumbold and Fink, 2006). Water flow rate and depth were managed as a means to alter sediment biogeochemistry and reduce in situ mercury methylation. Management included drying the marsh to prevent bioaccumulation in predatory fish and to reduce foraging by wading birds, followed by maintaining deeper water levels to reduce oxygen levels in bottom waters, reducing the production of sulfate and mercury methylation within surficial sediments. The exact biogeochemical mechanisms surrounding these anomalously high MeHg concentrations in STA-2, Cell 1, are not fully understood, but the series of operational steps taken highlight the difficulties of managing the STAs for MeHg.

Trends within the Holey Land WMA are represented by a single canal site that is hydrologically connected to wetlands where average wet season water levels have been maintained approximately 0.3 meters lower than they were in the early 1990s when LMB collections began (see Appendix 3B-1 of this volume).

Although median THg concentrations have not changed drastically over the POR at site HOLEY, a strong upward gradient occurred during 1998–2006, when median LMB THg concentrations increased from 0.40 ppm (range: 0.11–0.80 ppm, $n = 20$) to 0.96 ppm (range: 0.67–1.30 ppm, $n = 20$) (**Figure 3B-12**). The effects of decreased water depths and more frequent drying and re-flooding cycles on bioaccumulation of mercury are unknown; however, median LMB THg concentrations have decreased in each of the last three years (2007–2009), while water level regimes have not changed. Similarly, mosquitofish and sunfish THg concentrations decreased 49 and 6 percent, respectively, from 2008 to 2009 (see Appendix 3B-1 of this volume).

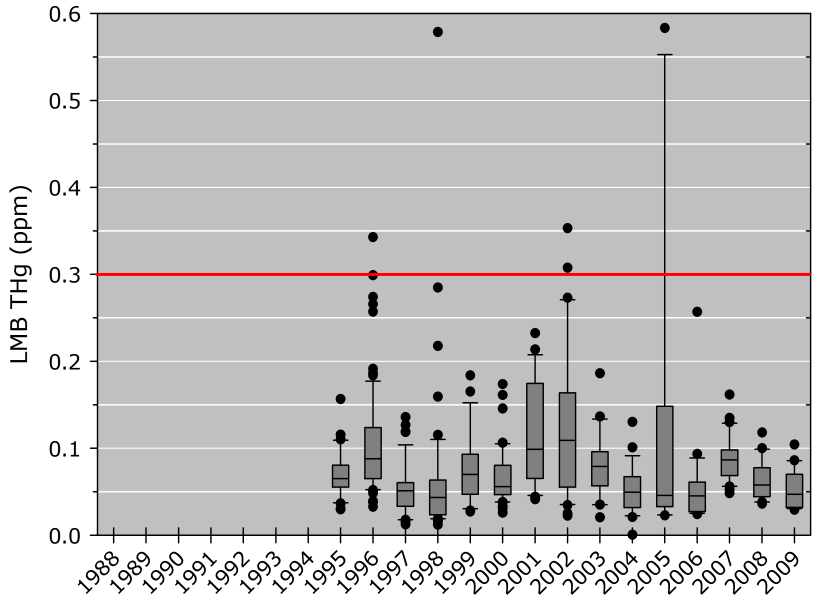


Figure 3B-11. Annual summaries of mercury concentrations (normalized to total fish length = 356 mm) in LMB collected from sites ENR003 and ENR012 in STA-1W, Cell 3, from 1995–2009.*

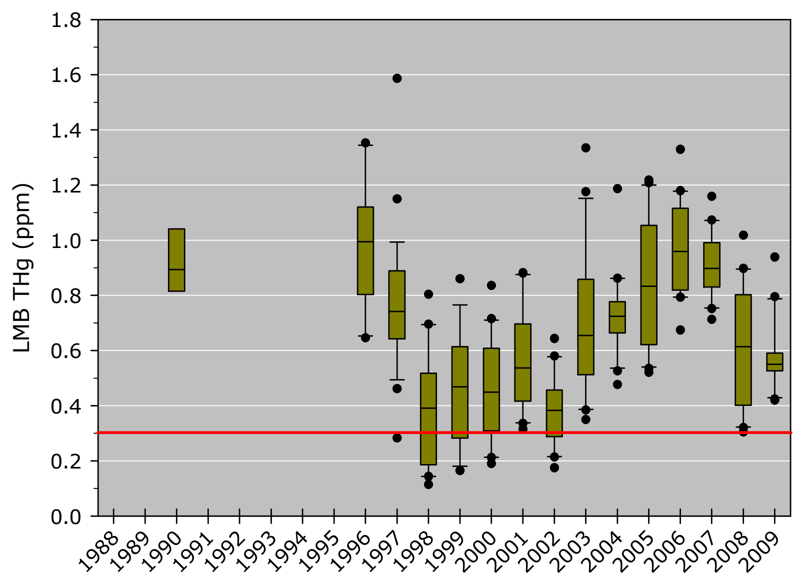
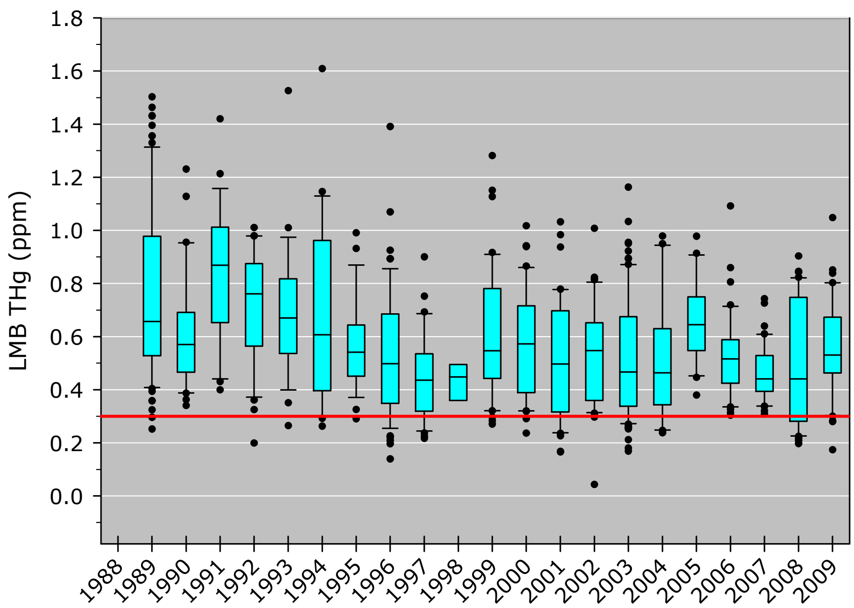


Figure 3B-12. Annual summaries of mercury concentrations (normalized to total fish length = 356 mm) in LMB collected from the north borrow canal (site HOLEY) within Holey Land WMA from 1990–2009.*

*Box plots represent the median, 25th, and 75th percentile; whiskers the 10th and 90th; and points are outliers. The 0.3 ppm USEPA MeHg criterion is indicated in red.

In the Northern Everglades region, mercury continues to be a significant water quality issue. The FDEP lists 11 water bodies within the Kissimmee Basin as impaired due to mercury, and the FDOH (2009) has advisories recommending limited consumption for 12 species of fish in the KCOL. The FDOH further advises that anglers not consume LMB from several lakes not part of the KCOL but that are within the Kissimmee Basin, including the Kissimmee River. Previous SFERs (e.g., Gabriel et al., 2010a) listed a range of THg data for various sport fish from 13 lakes and the Kissimmee River. For this year's report, data from 803 LMB collected in 21 sampling events from 1989–2010 are summarized as pooled annual medians for Lakes Kissimmee, Tohopekaliga, and East Tohopekaliga (part of the KCOL) to provide insight into temporal trends and to contrast to mercury concentration levels within the (downstream) EPA.

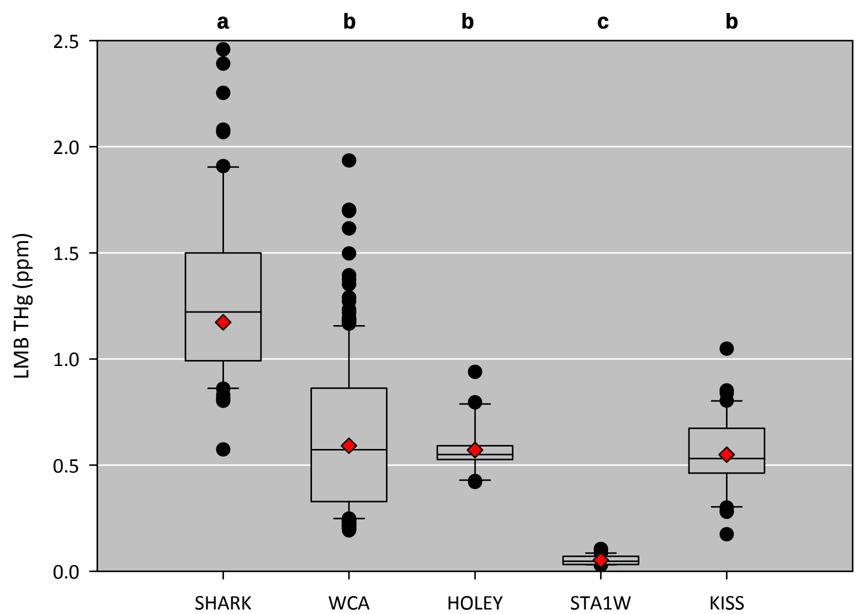
Median THg concentrations were maximal during initial sample collections within the Northern Everglades region. In 1991, the median was 0.87 ppm (range: 0.40–1.42 ppm, n = 29) and declined steadily to the lowest level in 2008 with a median of 0.44 ppm (range: 0.20–0.90 ppm, n = 40), a 49 percent decrease (**Figure 3B-13**). A seasonal Kendall analysis indicated a significant (r = -0.448; p = 0.005) 14 percent decline in THg concentrations in LMB. Although this trend seems promising, as of 2009, THg levels in LMB and other large-bodied piscivorous fish remain at or above the USEPA MeHg criterion for the protection of human health throughout the entire Kissimmee Basin.



Box plots represent the median, 25th and 75th percentile; whiskers the 10th and 90th; and points are outliers. The 0.3 ppm USEPA MeHg criterion is indicated in red.

Figure 3B-13. Annual pooled summaries of mercury concentrations (normalized to total fish length = 356 mm) in LMB collected from Lakes Kissimmee, Tohopekaliga, and East Tohopekaliga from 1989–2009.

Shark River Slough in the ENP has replaced site CA315 as the most significant Everglades mercury hot spot (see the *Fish in the Everglades Protection Area* section of this chapter). In spite of Shark River Slough having aqueous MeHg concentrations up to 60 times lower than in areas to the north in the WCAs (USEPA, 2001b), Shark River Slough LMB were significantly higher in THg ($p < 0.05$) than LMB in all other regions in 2009. Similar to previous years, a south-to-north, high-to-low gradient in THg in LMB was evident with significant differences [analysis of variance (ANOVA); $F_{4,298} = 59.40$; $p < 0.001$] observed among regions within the Greater Everglades (**Figure 3B-14**). Shark River Slough had significantly higher (t-statistic = 6.750 to 15.098; $p < 0.001$; df = 4) and STA-1W, Cell 3, significantly lower (t1 = 7.230 to 15.098; $p < 0.001$; df = 4) THg in LMB than the WCA and Holey Land WMA regions. The lakes tested within the Northern Everglades region were intermediate in THg levels.



Note: Adjusted least square means are indicated in red and are not significantly different when letter designations are the same (analysis of variance).

Figure 3B-14. LMB median mercury concentrations from Shark River Slough (SHARK), WCAs 1, 2, and 3 (WCA), Holey Land WMA (HOLEY), STA-1W, Cell 3 (STA1W), and Northern Everglades (KISS) regions during the 2009–2010 sampling period.

EVERGLADES SULFUR LEVELS, SOURCES AND EFFECTS

Elevated concentrations of both mercury and sulfur are evident in the Everglades, with mercury sourced predominantly from atmospheric deposition, and sulfur probably from agricultural activities. Excessive mercury levels in high trophic level Everglades fish are related to elevated sulfur concentrations; naturally occurring sulfate reducing bacteria convert inorganic mercury into MeHg.

Evaluating the efficacy of reducing sources of sulfur to the Everglades as a means of reducing mercury in fish is an important step in water quality restoration efforts. Mercury atmospheric deposition to South Florida remains high relative to that for most of the United States. (NADP, 2010); however, this deposition is now predominantly from global (international) rather than local (within Florida) sources (Atkeson et al., 2005; Axelrad et al., 2007 and 2008; Pollman et al., 2007). Since reducing global mercury sources is not feasible in the short term, reducing sulfur loading to the Everglades from agricultural activities (Axelrad et al., 2007 and 2008; Gabriel et al., 2008 and 2010a; Orem et al., in press), may be the most practical means of lowering MeHg levels in Everglades fish.

Sulfate originating from the Everglades Agricultural Area (EAA) may be stimulating MeHg bioaccumulation in EPA fish. Beyond mercury methylation, sulfur is a concern because (1) as sulfate or sulfide it affects the biogeochemical cycling of numerous elements, and may promote the release of phosphorus (a nutrient of concern) from sediments; and (2) as sulfide, it is toxic to aquatic plants and animals.

EVERGLADES MERCURY CONCENTRATIONS LINKED TO SULFUR

In the 1980s, Florida state agencies monitoring mercury levels in freshwater fish state-wide, were surprised to find that of 80 Florida water bodies monitored for mercury through LMB sampling, the Everglades had the highest mercury concentrations. Largemouth bass in the central Everglades (WCA-3) had mean values of 2.7 ppm THg (Ware et al., 1990). For water bodies without direct input of mercury from industrial activity or mining runoff, this mercury level in Everglades fish was among the highest reported in fresh waters worldwide.

At the time, this finding of high mercury concentrations was puzzling because the Everglades is relatively distant from industrial activity. However, it was quickly determined that the mercury sourced to the Everglades was almost entirely (> 95 percent) from wet (rain) and dry (particulate mercury) atmospheric deposition (Landing et al., 1995; Pollman et al., 1995; Stober et al., 1996, 1998, and 2001; Guentzel, et al., 1998 and 2001).

Consequently, in the early 1990s, pollution controls were implemented on emissions to the atmosphere from South Florida municipal waste combustors and medical waste incinerators. Mercury levels in fish subsequently declined substantially (about 60 percent to date) in Everglades WCAs (Gabriel et al., 2010a; see also the *Fish in the Everglades Protection Area* section of this chapter). To date, mercury levels in Everglades LMB remain generally higher than the USEPA MeHg fish tissue criterion (0.3 ppm MeHg) for protection of human health from consumption of fish. In addition, mercury levels in Everglades fish also pose risks to fish-eating wildlife (Rumbold et al., 2008; see also the *Mercury in Everglades Wildlife and Fish* section of this chapter).

Despite some mercury concentration declines, mercury-in-fish hot spots (THg > 1 ppm in LMB) remain, and these areas have shifted around in the Everglades over time, possibly more as a consequence of changing biogeochemistry than a changing rate of atmospheric deposition of mercury (Axelrad et al., 2005).

A second surprise regarding Everglades water quality was the discovery of high levels of sulfur in surface waters and sediments (Orem et al., 1997). U. S. Geological Survey (USGS) investigators sampling at a site in WCA-2A in the mid-1990s were struck by the strong "rotten egg" odor of hydrogen sulfide. High concentrations of hydrogen sulfide are unusual for freshwater wetlands — this is more characteristic of marine or estuarine systems with low dissolved oxygen concentrations. It was also evidence of microbial sulfate reduction.

Because sulfate-reducing bacteria (SRB) are important biomethylators of mercury, microbial sulfate reduction is clearly linked to mercury levels in fish (Compeau and Bartha, 1985; Ekstrom et al., 2003; Gilmour et al., 2004). Methylation of mercury produces MeHg, which is more toxic and bioaccumulative than inorganic mercury (Driscoll et al., 2007; Munthe et al., 2007). Therefore, the rate of mercury methylation by naturally occurring SRB is an important determinant of MeHg levels in fish. The MeHg in fish represents the dominant mercury threat to humans and wildlife that eat fish.

The balance between sulfate and sulfide is a key control on net mercury methylation rate in most ecosystems, including the Everglades. Sulfate stimulates methylation of mercury by SRB, but sulfide created from the reduction of sulfate leads to the formation of mercury-sulfur complexes that are less bioavailable for uptake and methylation by SRB (Benoit et al., 1999a; 1999b; King et al., 2001).

When sulfate is the limiting factor for sulfate reduction (as it is in the Everglades), the activity of SRB and the concomitant production of sulfide is a linear function of sulfate supply. However, most of the sulfide produced from sulfate reduction is rapidly bound up in organic matter and/or iron sulfides in sediments. Therefore, porewater sulfide concentrations are generally well below porewater sulfate concentrations. In the Everglades, organic matter is the main sink for sulfide. The balance between the activity of SRB and the resultant concentration of free sulfide in porewaters in an important control on MeHg production. The activity of SRB increases linearly with sulfate supply, while the bioavailability of mercury decreases with increasing sulfide (Munthe et al., 2007). Studies have shown positive correlations between MeHg production and surface water sulfate concentrations in the WCAs up to 20 ppm sulfate (Gilmour et al., 2007a); at porewater sulfide concentrations >1 ppm, sulfide becomes inhibitory to MeHg production (Orem et al., in press.) Raising sediment porewater sulfide concentrations beyond this in order to repress mercury methylation is, however, not an acceptable strategy, as sulfide may be toxic to Everglades flora and fauna (Li et al., 2009; Orem et al., in press; USEPA, 1986).

ENVIRONMENTAL SULFUR EFFECTS

The existing high level of sulfate loading to the Everglades is important because sulfur has myriad impacts on the ecosystem beyond stimulating the production of MeHg. Sulfide is toxic to aquatic plants (Mendelssohn and McKee, 1988; Koch and Mendelssohn, 1989) and animals (National Research Council, 1979). Because SRB are primarily responsible for producing MeHg from atmospherically deposited inorganic mercury, sulfur contamination has increased MeHg levels in Everglades fish (Axelrad et al., 2007; Gilmour et al., 2007b, Gabriel, 2009). Concerning plants, Li et al. (2009) hypothesized that sulfide toxicity could, in part, be responsible for the replacement of sawgrass (*Cladium jamaicense*) by cattail (*Typha* spp.) in the Everglades. Further research is being conducted on this topic (see the *Phosphorus Mobilization and Plant Toxicity Effects in Mesocosms Amended with Sulfate, Calcium and Alkalinity* subsection of this chapter).

Sulfate, via internal eutrophication, may cause the release of phosphorus and nitrogen from wetland soils (Axelrad et al., 2007; Lamers et al., 1998; Smolders et al., 2006). There is preliminary evidence of sulfate-induced internal eutrophication in the Everglades (Gilmour et al., 2007a), and further research is being conducted on this topic (see the *STA/WCA Internal Eutrophication Study: Interim Findings* section of this chapter).

Recent data (Orem et al., 2010) from northwest WCA-2A indicate that surface water levels of undissociated hydrogen sulfide are many times higher than the USEPA's water quality criterion [2 micrograms per liter (μg/L) or parts per billion (ppb)] for protection of fish and other aquatic life (USEPA, 1986). This is consistent with hydrogen sulfide data from surface waters from WCA-2A as reported in 1997 by Orem et al.

Of these detrimental environmental effects of sulfur, it is likely that increased MeHg production occurs at lower sulfate concentrations than does sulfide toxicity or internal eutrophication. Accurate estimates of Everglades sulfur sources, fate, and transport are needed to determine if it is feasible to reduce sulfur loading to a level that would bring lower MeHg in Everglades fish (to acceptable levels).

THE EVERGLADES AGRICULTURAL AREA AS SULFUR SOURCE TO THE EVERGLADES PROTECTION AREA

The EAA is adjacent to and directly south of Lake Okeechobee, and borders the Water Conservation Areas to the south and southeast (see **Figure 3B-6**). The EAA comprises approximately 700,000 acres, with about 430,000 acres in crop production; 350,000 acres of this is sugarcane, the remainder is made up of vegetables, sweet corn, rice, sod, and plant nurseries (UF/IFAS, 2006). Historically, the EAA was part of the Greater Everglades, but has been farmed since the partial drainage of the Everglades in the early 1900s (UF/IFAS, 2006). In 1948, the EAA was specifically designated for agricultural use, under the U.S. Army Corps of Engineers' (USACE) Central and South Florida Flood Control Project.

Due to its hydrological connection to the Everglades, the EAA is now managed to minimize the effects of some agricultural activities on the ecosystem. The 1994 Florida Forever Act (Section 259.105, Florida Statutes) requires farming practices that minimize phosphorus levels in water discharged from farmland to the Everglades (see Chapter 4 of this volume). Phosphorus, while an essential nutrient for crop growth, in excess amounts can be harmful to the Everglades, perhaps most notably by eliminating calcareous periphyton and causing the replacement of native sawgrass with invasive cattails. In addition to EAA farming best management practices to minimize phosphorus pollution, 40,000 acres of constructed wetlands, the STAs, have been developed to remove phosphorus from farmland runoff before it can enter the Everglades (see Chapter 5 of this volume).

Agricultural Sulfur and Regional Concentration Gradients

Like phosphorus, sulfur is a plant nutrient, and it has several roles in EAA agriculture. Possibly the greatest use of sulfur in the EAA is as a soil amendment for pH adjustment (Boswell and Friesen, 1993). Elemental sulfur acidifies soil, and by reducing soil pH, it increases the availability of phosphorus and micronutrients (trace metals) for crops. When soil pH exceeds 6.6 standard units (SU), recommendations are to apply 500 pounds per acre (lbs/acre) for muck and sandy mucks, 300 lb/acre for mucky sands, and no sulfur for sands (Rice et al., 2006). Actual sulfur use in the EAA is estimated to be 30–100 lbs/ac every three years (Wright et al., 2008).

Concentration gradients across the Southern Everglades implicate the EAA as the dominant source of sulfur to the ecosystem, though better identification and quantification of the underlying and proximate sources of sulfur in the EAA is needed. Everglades surface water sulfate concentrations follow a north-to-south gradient from the EAA to the freshwater ENP, with sulfate levels nearer the EAA often exceeding 100 times those in parts of the ecosystem further south and away from canal discharges (Bates et al., 2002; Gilmour et al., 2007b; Weaver et al., 2007).

Sulfate discharged from the EAA is not efficiently removed by the STAs since these constructed wetlands were created to reduce phosphorus entering the EPA (in large part through uptake of phosphorus by plants). The STAs were neither intended nor designed to remove the much higher levels of sulfate from EAA runoff, so while STA removal efficiency for phosphorus is about 70 percent, it is only about 10 percent for sulfate (Pietro et al., 2009). This is because the mass of inflow of sulfate/sulfur to the STAs exceeds that of total phosphorus by 1,000 to 1, while as nutrients, sulfur and phosphorus are required by plants — such as those in STAs — in about a 1-to-1 ratio (Beaton, 1966; Tabatabai, 1984).

The disparity in sulfate versus phosphorus loading to the Everglades through the STAs is evident. While about 30 percent of the area of surface waters in the Everglades marsh exceed the 10 ppb total phosphorus water quality standard, about 60 percent of the Everglades marsh exceeds the 1 ppm (1,000 ppb) sulfate/sulfur Comprehensive Everglades Restoration Plan goal (Scheidt and Kalla, 2007).

Sulfur concentration gradients and the extent of Everglades sulfur contamination have been documented by the USGS, the USEPA, and the SFWMD (Orem et al., 1997; Stober et al., 2001; Bates et al., 2001 and 2002; Scheidt and Kalla, 2007; Payne et al., 2009). Surface water sulfate concentrations in northern Everglades marshes can reach from about 40 to 70 mg/L in WCA-2 compared to ≤ 0.1 mg/L in parts of the ecosystem farther south and away from canal discharges (Bates et al., 2002; Orem, 2004; Gilmour et al., 2007a; Scheidt and Kalla, 2007). Sulfide in Everglades soil porewater shows a north-to-south gradient similar to that for sulfate in surface water, with extremely high sulfide concentrations in sediment porewater (up to 12,000 ppb) in the north and low concentrations (0.1 ppb) in the south.

Everglades Agricultural Area Sulfur Mass Balance and Soil Subsidence

There have been recent attempts at determining an EAA sulfur mass balance. Regarding agricultural applications of (elemental) sulfur in the EAA, Gabriel (2009) estimated that applications averaged 20 lbs/acre per year, based on a weighted mean of sulfur applied to various crop types. Wright et al. (2008) estimated agricultural applications at 33 lbs/acre per three years, based on the estimates of Schueneman (2001), which were derived from interviewing several EAA growers, as well as sellers of fertilizer in the EAA region. Oxidation of agricultural sulfur applied to EAA soils allows sulfate to be transported into EAA canals during rain events (Bates et al., 2002) from where it moves downstream to the EPA.

Another source of sulfur is oxidation of EAA soil (soil subsidence). Soil subsidence in the EAA occurs at an accelerated rate because these soils are highly organic and composed largely of decomposed sawgrass which accumulated under flooded, low-oxygen conditions over thousands of years. With the EAA being pumped dry to allow crop production (UF/IFAS, 2006), the resultant aerobic conditions led to the relatively rapid loss of organic matter in EAA soils via microbial oxidation, compared with the rate of soil loss in flooded and anoxic Everglades soils (Wright and Snyder, 2009). Gabriel (2009) reported that the EAA soil oxidation rate resulted in soil losses ranging from 0.5 to 1.5 inch/year, while Wright et al. (2008) and Wright and Snyder (2009) reported recent EAA soil oxidation rate to be about 0.5 inch/year. Schueneman (2001) also used the 0.5 inch/year soil oxidation rate for sulfur mass balance estimates. Similar to agricultural sulfur applications, soil subsidence (microbial oxidation of soil organic sulfur) also releases sulfate to the EPA via EAA canals during rain events.

Several EAA sulfur mass balance estimates vary as to their assessments of the relative importance of soil oxidation versus agricultural sulfur application as sources of sulfur to the Everglades. Gabriel (2009) estimated that sulfur released from EAA soil oxidation exceeded sulfur from agricultural application by a factor of 5, while Wright et al. (2008) estimated that ratio at 11, and Schueneman (2001) estimated the ratio at 15 (Gabriel et al., 2010a). Estimates vary greatly because of uncertainties in the actual amounts of all forms of sulfur added to EAA soils, average sulfur contents, and oxidation rates of EAA soils.

The source of the sulfur in EAA soils has a bearing on potential options for reducing sulfur loading to the Everglades. Gabriel (2009) notes that total sulfur concentrations range from 0.1–5 percent in soils across the EAA. Organic sulfur, the largest fraction of the total sulfur in peat soils from the freshwater Everglades, accounts for 50–85 percent of the total sulfur at most locations (Altschuler et al., 1983; Bates et al., 1998; Ye et al., 2010a). Organic sulfur forms through the reaction of sulfide with soil organic matter, and thus it is plausible that some or even most of the organic sulfur in EAA peat soils results from the reaction of agricultural applications of sulfur with soil organic matter (Bates et al., 2002).

Results of isotope and other studies are consistent with the conclusion that agricultural sulfur applied to EAA soils is an important source of sulfur to the EAA soil organic sulfur pool. Sulfate from agricultural sulfur and soil oxidation (soil subsidence) enter the Everglades through canal discharge (Bates et al., 2002; Orem, 2004; Axelrad et al., 2007; Gilmour et al., 2007a; Gabriel et al., 2008).

In addition to agricultural sources within the EAA that create a high sulfur load in the region, Lake Okeechobee is a significant source of sulfur to the EAA (Gabriel et al., 2010a) even though it has annual average sulfate concentrations less than half of those in EAA canals (Bates et al., 2002). The lake receives sulfur from EAA backpumping, as well as from surface water runoff from upstream and adjacent agricultural lands (McCormick and James, 2008). Sulfur loading to the EAA from rainfall and groundwater are estimated to be low (Axelrad et al., 2007 and 2008; Gabriel et al., 2010; Gilmour et al., 2007a; Orem et al., in press).

Existing data support the hypothesis that the EAA is the principal source of sulfate to the Everglades, and that sulfur sourced from EAA agriculture, which includes new sulfur soil amendments plus sulfate released via oxidation of EAA soils (soil subsidence), is the principal source of sulfate to EAA canals that discharge to the EPA.

IMPACTS OF SULFATE LOADING TO NORTHWESTERN WATER CONSERVATION AREA 2A AND EVERGLADES NATIONAL PARK

In 2008, the USGS and other partners began examining the interactions of sulfate, mercury, and dissolved organic carbon (DOC) in northwestern WCA-2A and the ENP. This section describes the sampling and overall findings of these recent efforts.

Northwestern Water Conservation Area 2A

One area of the Everglades where sulfate loading has changed dramatically over the last decade is northwestern WCA-2A. Garrett and Ivanoff (2008) documented increased sulfate loading to this area due to the opening of STA-2 in July 2001. Historically, the northwest section of WCA-2A received water via the S-10E structure, but the structure was closed in 1997, causing rainfall to be the primary source of water to the northwest section of WCA-2A. Beginning in July 2001, treated water from STA-2 was released into the northwest section of WCA-2A. Prior to this opening, sulfate concentrations in northwestern WCA-2A ranged from 5–17 ppm, but concentrations since then have averaged about 61 ppm (Garrett and Ivanoff, 2008).

In 2009–2010, the USGS began an examination of the impacts of sulfate loading from canal water releases in the WCA (Orem et al., 2010). Sampling of surface water, porewater, and soil was conducted in August–September 2009 and February 2010, at the same sites used by Garrett and Ivanoff (2008). The observed sulfate levels ranged from 60–80 ppm in surface waters at the 10 sites, which is similar to values observed by Garrett and Ivanoff (2008). Sulfide levels in porewaters ranged from 7–6,000 ppb.

Sulfate loading stimulates microbial sulfate reduction, which results in increased sulfide levels in sediment porewater. The sulfide levels observed in northwestern WCA-2A were not high enough to be toxic to sawgrass (Li et al., 2009), but sulfide may increase to levels toxic to plants if the high sulfate loading rates to this area are maintained. Total sulfide levels in surface water ranged from 7–307 ppb, which is equivalent to about 3.5–153 ppb of undissociated hydrogen sulfide at the observed field-measured surface water pH (between 7 and 8 SU). All sites sampled in northwestern WCA-2A exceeded the USEPA surface water standard (2 ppb undissociated hydrogen sulfide) recommended to protect aquatic fauna and flora (USEPA, 1986).

THg levels in surface water ranged from 0.8–4.3 nanograms per liter (ng/L), typical of surface water levels throughout the ecosystem (Scheidt and Kalla, 2007). In contrast, MeHg levels in surface water in northwestern WCA-2A in 2009–2010 were elevated at some sites. MeHg levels ranged from 0.04–1.1 ng/L (mean and median of 0.33 and 0.22 ng/L, respectively), but with a number of sites having levels of MeHg > 0.4 ng/L. These high values likely reflect the production of MeHg due to enhanced rates of sulfate reduction. Sites with lower levels of MeHg tended to have higher sulfide levels, indicative of the balance between stimulation of mercury methylation by sulfate and inhibition by sulfide (Axelrad et al., 2007).

High levels of DOC are also present in northwestern WCA-2A, with concentrations in surface water ranging from 27–47 ppm. High DOC levels may be partly linked to the discharge of DOC-enriched canal water from STA-2, and partly due to sulfate enhancement of microbial organic matter decomposition. High DOC may enhance the methylation of mercury by complexing mercury, making it more bioavailable to methylating microbes. Studies are ongoing.

Everglades National Park

In October 2008 and 2009, the USGS and the NPS collaborated to sample 76 sites across the ENP for sulfur and mercury (Krabbenhoft et al., 2010). The objective was to examine whether there was any evidence to link canal water releases from the S-12 canal and the L67 terminus along the northern ENP boundary with water quality changes in the ENP. Since surface water releases generally follow the Shark River Slough, the hypothesis was that several water quality indicators would be correlated with canal water releases.

At each site, surface water and small fish were collected. Water samples were analyzed for general water quality parameters, sulfate, DOC, THg, and MeHg. Results from both years were similar. Compared to the other analytes, THg concentrations exhibit relatively little variability across the ENP, with modestly higher concentrations seen in the S-12 and L-31W canals and Shark River Slough. The relatively small amount of THg variability is likely due to the uniform deposition pattern of atmospheric mercury that occurs across the Everglades, as evidenced by the Mercury Deposition Network data (http://nadp.sws.uiuc.edu/mdn/; Krabbenhoft et al., 2008).

Methylmercury showed a different pattern, with elevated levels (generally 0.25–1.0 ng/L) observed in Shark River Slough. Much lower MeHg concentrations (generally less than 0.1 ng/L) are seen in areas of the ENP where the presence of canal water is not apparent (determined by sulfate and fluoride markers), such as the Rocky Glade area. Samples collected from the S-12/L-31W region generally show MeHg concentrations that are between levels from Shark River Slough and Rocky Glade. One of the most striking results from these two sampling efforts were those from the lower C-111 canal, which revealed some of the lowest MeHg levels ever observed by the USGS, and appear to be the result of abnormally (for the Everglades region) low DOC levels observed at this location. Much like the results from northwestern WCA-2A, there is a sulfate concentration optimum for mercury methylation in the ENP, though this occurs at lower sulfate concentrations than for WCA-2.

For the ENP dataset, low sulfate concentrations (less than 1 ppm) were associated with a substrate limitation response (meaning that mercury methylation by SRB was limited by the amount of sulfate), and high sulfate concentrations (greater than about 5 ppm) were associated with an inhibition effect, presumably due to sulfide accumulation in porewater, causing reduced mercury bioavailability. At mid-level sulfate concentrations (1–5 ppm), MeHg production appears to be maximal in the ENP. MeHg in mosquitofish tissue exhibited a spatial pattern that agreed very closely with the aqueous MeHg results.

In summary, results from this study suggest that MeHg production in the ENP reacts to sulfate loading similarly to previously studied regions of the Everglades, but with a different range of optimum sulfate concentrations (compared with WCA-1, WCA-2, WCA-3, and BCNP). Restoring water flow to the southern portions of the Everglades is a key goal of the restoration effort in South Florida, but surface water quality also needs to be considered when conducting a complete environmental benefit analysis.

ELEMENTAL SULFUR USE FOR SUGARCANE PRODUCTION IN THE EVERGLADES AGRICULTURAL AREA

As a result of the conversion of EAA lands from seasonally flooded wetlands to agricultural use, soil subsidence has occurred and continues at a rate of about 0.6 inches/year (Shih et al., 1998; Wright and Snyder, 2009). In 1912, much of the EAA had soils thicker than 120 inches. By 1988, only 17 percent of the EAA had soil thicker than 51 inches, while 53 percent had soils less than 36 inches thick, and 11 percent had soils less than 20 inches thick (Scheidt and Kalla, 2007).

After almost a century of farming in the EAA, the depth of soil has declined in some areas to the point where cultivation, specifically tillage, has resulted in the incorporation of EAA limestone-bedrock into peatland EAA soils. Sugarcane lands especially require multiple tillage applications before and during the growing season.

The limestone bedrock that underlies EAA soils is composed of calcium carbonate ($CaCO_3$), which has high pH when dissolved in deionized water. Incorporation of EAA $CaCO_3$ bedrock into EAA soils through tillage and as a result of declining soil depths has increased the soil pH over time (Snyder, 2005; Gabriel et al., 2008). These soil pH increases have decreased phosphorus and micronutrient availability to crops and may require new fertilizer management practices (Ye et al., 2010a, b).

Application of elemental sulfur (agricultural sulfur) to EAA soils has long been recommended as a means to reduce soil pH when it exceeds 6.6 SU, for purposes of lowering pH and improving the availability of soil phosphorus and micronutrients (trace metals) to sugarcane (Anderson, 1985; Schueneman, 2001). Recommendations are 300–500 lbs/acre of agricultural sulfur for highly organic EAA soils (Rice et al., 2006), although actual use is estimated at much lower rates (see the *Everglades Agricultural Area Sulfur Mass Balance and Soil Subsidence* section of this chapter). The natural microbial oxidation of the added elemental sulfur produces sulfate, reduces soil pH, and enhances phosphorus and micronutrient release from soil. This, in turn, increases phosphorus and micronutrient availability to crops, increasing plant productivity.

In response to increasing soil pH, elemental sulfur application to EAA soils is being evaluated for its current influence on soil chemical and microbiological properties (Ye et al., 2010a). During the first two months after application, sulfur additions at the highest rate, 400 lbs/ac, did increase phosphorus concentrations in the iron-aluminum-bound phosphorus fraction by 55 percent compared to unamended soils (Ye et al., 2010b). The stimulatory effects of this elemental sulfur addition on phosphorus release were quite limited however, possibly because the iron-aluminum-bound phosphorus fraction averaged only 4 percent of soil total phosphorus. Furthermore, the stimulatory effects did not last beyond two months. Similar to labile phosphorus, water-extractable potassium and acetic-acid-extractable zinc increased by 71 and 134 percent, respectively, only during the first two months after adding elemental sulfur at the highest rates, then the stimulatory effects ceased (Ye et al., in press).

Similar to the effects on soil chemical properties, elemental sulfur promoted short-term changes in soil microbial activities. The activities of phosphatase and glucosidase in soils receiving 400 lbs/acre were 115 and 560 percent higher, respectively, than in unamended soils at two months (unpublished data). Microbial respiration and nitrogen and phosphorus mineralization rates were not affected by elemental sulfur amendment, suggesting that application under the current recommendations would not enhance soil subsidence and release rates of nitrogen and phosphorus.

Extractable sulfate in soils receiving 400 lbs/acre was 36, 131, 201, and 270 percent higher than unamended soils at 2, 6, 9, and 13 months, respectively (Ye et al., 2010a). Both extractable sulfate and dissolved organic sulfur decreased throughout the growing season, likely due to uptake by sugarcane, but also potentially by runoff or leaching through the shallow soils. Elemental sulfur was not detected in unamended soils, and its concentration in amended soils gradually decreased throughout the growing season, but it was still detected in soil at 13 months after application (Ye et al., 2010a).

Agricultural sulfur application in a Dania series soil using current recommended guidelines (up to 400 lbs/ac) did not increase sugarcane yield. There may be a need for greater agricultural elemental sulfur application rates in some EAA soils to overcome the soil's buffering capacity, and thus release phosphorus. Sulfur application rates above 400 lbs/acre could continue to reduce soil pH and cause releases of phosphorus from the calcium-bound fraction (Gessa et al., 2005). Calcium-bound phosphorus comprises 32 percent of total phosphorus and more than 80 percent of total inorganic phosphorus in EAA soils.

It is important to note that the EAA sulfur amendment recommendations were developed many years ago, before the occurrence of widespread increases in soil pH due to soil subsidence. Thus, the effectiveness of elemental sulfur amendment for the higher pH soil conditions in the EAA has been questioned (Schueneman, 2001; Ye et al., 2010b). Additional evaluation of the effectiveness of elemental sulfur use for sugarcane grown on various soil types with higher pH values within the EAA is ongoing.

INFORMATION NEEDS AND RECOMMENDATIONS

Information needs and recommendations regarding Everglades sulfur source determination and management include:

1. Better estimating Everglades, Lake Okeechobee, and EAA sulfur mass balances, including quantifying agricultural application of sulfur to soils in the EAA and applications previously not measured [e.g., addition of gypsum ($CaSO_4$) for EAA soil erosion control].
2. Accurately determining the rate of oxidation of EAA soil organic sulfur, for dry and submerged-soil conditions.
3. Determining the relative contributions of natural and agricultural sulfur to organic sulfur in EAA soils.
4. Determining the time for sulfur release from EAA soils to reach a steady-state value after cessation of agricultural applications of sulfur.
5. Assessing soil depths across the EAA and total sulfur stocks within the EAA.
6. Measuring groundwater sulfur inputs to the EAA.
7. Implementing high-resolution spatial sampling frameworks over various time periods to capture particular meteorological conditions (i.e., dry, wet, and intermediate seasons) with

more frequent measurement of sulfur flux occurring at water structures in the Everglades to better determine sulfur inputs to various areas of the ecosystem (Gabriel, 2009).

8. Modeling the response of mercury levels in Everglades fish to sulfate concentrations to estimate the reduction in sulfate loading to the ecosystem necessary to achieve desired fish mercury reductions.
9. Reviewing options for restoring the Everglades hydropattern while minimizing sulfur effects:
    - The delivery of sulfate-contaminated water through the Everglades canal system to protected areas such as the ENP and the Refuge — areas that previously did not have elevated levels of sulfur — may cause environmental harm. In contrast to transporting water though the canal system, moving water as sheetflow over expansive marsh areas may allow for sequestration of reduced sulfur in soils and thus reduce the sulfate loads delivered to these protected areas (Orem, 2007).
    - Current management practices have altered the Everglades natural drying and rewetting cycles: soil drying results in the oxidation of reduced sulfur to sulfate; upon rewetting, pulses of sulfate reduction and MeHg production occurs (Gilmour et al., 2004; Orem, 2007).
    - Reviewing the potential effects of Aquifer Storage and Recovery on Everglades sulfur loading (Krabbenhoft et al., 2007).
    - Estimating the cost and effectiveness of sulfur Best Management Practices for the EAA and the Lake Okeechobee Watershed.
    - Continuing to evaluate effectiveness of agricultural sulfur application for enhancing crop production, and alternatives to sulfur application to EAA crops so as to maintain high crop production rates while minimizing environmental impact (e.g., phosphorus addition; alternative means of lowering soil pH).

RESEARCH PROGRESS

The following research needs were identified in peer-review comments from previous Everglades Consolidated Reports (ECRs) and *South Florida Environmental Reports* (SFERs) – *Volume* I for the mercury chapter. Updates on progress follow. These projects address sources, toxicity, and biogeochemistry of mercury and sulfur, as well as prediction (modeling) of the effects of implementing mercury or sulfur source reduction on the ecosystem.

1. **Quantify the no-effect level for Greater Everglades fish-eating bird dietary exposure to MeHg to support development of a water quality criterion (2000 ECR).**

   Experimental exposure of white ibis (*Eudocimus albus*) to MeHg through diet significantly reduced reproduction. These effects were seen over a concentration range from the very high MeHg levels that existed in the Everglades in the early 1990s and in the ENP at present, down to current ambient MeHg levels in the WCAs. The main loss of reproduction was due to a high rate of MeHg-induced white ibis male-male pairings (up to 55 percent of males), an effect which was dose-related in two of the three study years (Frederick and Jayasena, 2008).

   Following the FDEP's initial support for research on MeHg effects on white ibis (Frederick et al., 2005, 2007; Axelrad et al., 2008, 2009), the U.S. Fish and Wildlife Service and the U.S. Army Corps of Engineers (USACE) provided continuing funding. The final report to the USACE was submitted in December 2008 (Frederick and Jayasena, 2008).

   In this study, experimental groups of 40 white ibises (even sex ratios) were exposed to 0.05, 0.1, and 0.3 mg MeHg/kg wet weight in diet from 90 days of age through three breeding seasons. No effects were found of MeHg on mass, size, survival, appetite, juvenile hormone levels, or the ability to learn to feed in novel situations.

   However, all of the mercury-dosed groups had significantly lower reproductive success than the control group in all years, with up to 30 percent reduction in reproductive success. The main loss of reproduction was due to nests not producing eggs, and this stemmed directly from a high rate of male-male pairings (up to 55 percent of males), an effect which was dose-related in two of the three years.

   The male-male pairings showed nearly all of the characteristics of male-female pairings, including phenology, courtship, copulation, nest construction, nest attendance, mate defense, and socially monogamous behavior. Male-male pairs were often of longer duration than male-female pairings, and dosed groups all had significantly more time (pair-days) spent in male-male pairings than did the control group. In all years, the majority of the reproductive deficits in dosed groups were attributable to male-male pairing (2006: 75–85 percent, 2007: 82–100 percent, 2008: 50–100 percent).

   Male-male pairings were not a result of location effects, sex ratio, or constrained mating opportunities. Additionally, male-male pair bonds in all groups were formed relatively early in the breeding season at a time when there were unpaired females available in breeding condition.

   Males that were dosed, and especially those that later paired with males, had significantly lower display rates than control males (Frederick and Jayasena, 2010). It seems likely that although females approached them for courtship, the displays of these males may have been substandard. Some homosexual males later formed heterosexual pair bonds in the same or subsequent seasons, and had fertile eggs in all of those situations, demonstrating that they were competent mates. Male-male pairings declined over the three breeding seasons, suggesting that birds were switching mates because of poor reproductive success.

   Expression of sex steroids (estradiol and testosterone) were also affected by MeHg exposure, showing a dose-dependent response (Frederick, UF, personal communication). The pattern of altered expression was exaggerated within any group among homosexual males, suggesting that MeHg-induced changes in hormone expression affected sexual behavior such as display rates and pairing preference, and through that mechanism, reproduction was affected. While this experimental evidence strongly links hormones, mercury exposure, and behavior, the physiological mechanisms involved are unknown.

This study suggests that MeHg can function as an endocrine disruptor, resulting in altered sexual behavior and reduced reproductive success. The reduction in reproduction was not trivial — if the normal sex ratio in the wild is 1:1, the reduction in success could be up to 55 percent (the proportion of males pairing with males in this study). In many studies, effects seen in the lab (or aviary) are exaggerated in the field because of additional stressors in the wild; it is unclear whether effects documented in the aviary would be exacerbated in the Everglades.

At minimum, the implications of this study are that MeHg exposure at ambient levels in the Greater Everglades in the early 1990s could have been enough to affect breeding behavior to the extent that measurable demographic change may have been realized. As mercury exposure declined in the late 1990s, the numbers of breeding pairs of wading birds increased by 3–5X. While some of this increase was clearly due to better hydrological conditions, hydropattern does not explain all of the increase, and mercury is an explanatory variable in nearly all models of population response during this period (Frederick and Jayasena, 2008). While these results are merely correlational, the experimental research demonstrates an effect and a mechanism by which mercury affected populations.

In addition, it is worth noting that the lowest effects level (0.05 mg MeHg /kg in diet) from this study is still commonly encountered by birds in the Greater Everglades today, while the highest effects level (0.3 mg MeHg/kg in diet) may presently be encountered by birds in the ENP. A CERP goal is to restore wading bird numbers in the ENP — historically the area of highest bird numbers in the Everglades — via hydrological restoration of the ENP. MeHg, however, appears to have a potentially powerful effect on reproduction in birds, and the effects research indicates it could strongly interact with other variables (e.g., hydrological restoration) to produce both masking and additive effects.

2. **Quantify "global versus local" atmospheric Hg sources to South Florida to better define options for reducing mercury levels in Everglades biota (2002 ECR).**

   See the *State-wide Mercury Total Maximum Daily Load Program* section of this chapter.

3. **Revise the Everglades Mercury Cycling Model (E-MCM) to include relationships between sulfur concentrations and mercury dynamics (2001 ECR).**

   The FDEP and the SFWMD have supported efforts to capture the biogeochemical relationships between the mercury and sulfur cycles in the Everglades Mercury Cycling Model (E-MCM), a mechanistic simulation model that runs on Windows™-based computers (Tetra Tech, 1999a, b; 2002). Results are reported in the 2010 SFER and by Gilmour et al. (2008). Additional statistical analyses using R-EMAP data to better elucidate the non-linear role of sulfate on methylation and mosquitofish mercury concentrations (and the migration of the so-called "sulfate Goldilocks region," which results in mercury-in-fish hot spots) have been proposed by the FDEP.

   A study funded by the Electrical Power Research Institute (EPRI) to improve the treatment of several processes in the lake version of the MCM (D-MCM) continues (see the 2010 SFER). EPRI also has approved funds to extend D-MCM to be more generalized so that users can simulate single-cell or multi-cell scenarios without having to modify or manipulate the source code in the model. In addition to having the ability to simulate lakes, rivers, and large water bodies, the new version of D-MCM is expected to be able to simulate large complex systems like the Everglades that contain both wetland and more purely aquatic cells.

4. **Research biogeochemical controls on mercury methylation (2001 ECR).**

   ACME Phase III Research: Significant progress has been made in understanding biogeochemical controls on mercury methylation through Aquatic Cycling of Mercury in the Everglades (ACME) Phase I and II research conducted by the USGS and the Smithsonian Environmental Research Center (SERC), through support by the USGS, the FDEP, and the SFWMD. Findings are detailed in USGS (2010).

   This research, begun in 2008, focused on the ENP, BCNP, and the Loxahatchee National Wildlife Refuge and has been extended at least until the end of 2011, with additional cruises planned in the Shark River Slough and the offshore marine zone.

   This project seeks to expand the knowledge of the factors controlling MeHg production in the Everglades, with specific attention to geographic areas where Everglades restoration may affect MeHg production and bioaccumulation. Because work under ACME Phases I and II was largely conducted in the WCAs, efforts for ACME Phase III will be in Everglades areas where less research has been conducted, particularly on federally managed lands.

   The overall objective of this next phase of research is to extend the understanding of interactions between mercury, sulfate, and DOC as they influence MeHg production in areas of the Everglades that are anticipated to receive increased water delivery from sulfate-rich EAA runoff or high-sulfate Aquifer Storage and Recovery waters.

   ACME Phases I and II Database and Data Synthesis: The FDEP contracted with SERC for completion of compilation and synthesis of ACME Phases I and II data. The SERC data compilation will include a detailed assessment, through time, of the biogeochemistry of core ACME Phase I and II sites across the full length of the Everglades ecosystem and compile data from field mesocosm experiments designed to test cause-and-effects hypotheses.

   This project is planned to compile data from all ACME researchers in one central database where it can be queried and studied as controls on sulfur inputs to the Everglades are debated; a text report on the synthesized dataset is also planned. As part of that report, a synthesis of the literature on MeHg production with a detailed focus on studies of the relationship between sulfate, sulfide, and MeHg will be produced. The literature summary will help to put the ACME datasets into a larger context, and provide information to decision makers. Metadata will also be included. The dataset is slated for public accessibility (as well as submitted to the USGS for consideration for publication as an open file report).

5. **Determine sulfur sources to and effects on the Everglades (2006 SFER).** See the *Sulfur Levels, Sources and Effects on the Everglades* and *Regional Sulfur Mass Balance Study* sections of this chapter.

STATE-WIDE MERCURY TOTAL MAXIMUM DAILY LOAD

By 2012, the FDEP is required to develop a draft mercury Total Maximum Daily Load (TMDL) for mercury-impaired fresh waters of the state for review by the USEPA. In 2008, the FDEP initiated a multiyear statewide mercury TMDL study for fresh water that includes both atmospheric and aquatic field monitoring and modeling components. The mercury TMDL study is described in the 2010 SFER – Volume I, Chapter 3B.

MERCURY IN COASTAL WATERS

On a national scale, Americans are exposed to MeHg almost exclusively through the consumption of fish. Approximately 5 percent of women of childbearing age in the United States have blood MeHg levels that pose an increased risk to fetal brain development (Mahaffey et al., 2009). Many states are implementing mercury TMDLs to mitigate exposure to MeHg, but currently these TMDLs are being derived predominantly for fresh waters. The entire Atlantic and Gulf of Mexico (Gulf) coasts of the United States are under limited or no-consumption advisories for fish. Florida alone lists over 60 fish species of commercial or sport-fishing interest from the Gulf as under these advisories because of mercury content (FDOH, 2009). Marine and estuarine fish (finfish, shellfish, and crustaceans) make up more than 90 percent of the total fish consumption and MeHg exposure, indicating an obvious need for marine TMDL development. Less than 10 percent of fish eaten are from fresh waters (Degner et al., 1994; Sunderland, 2007).

The FDEP is initially addressing mercury in the Gulf because it is a very significant fishery — accounting in 2008 for 15 percent of the nation's marine commercial fishing, and 42 percent of the marine recreational fish catch (NOAA, 2010a, b). Because MeHg levels in a high proportion of fish in the Gulf exceed the proposed USEPA fish tissue criterion for human consumption, the Gulf is a significant source of human exposure to MeHg.

Determining the feasibility of reducing elevated MeHg concentrations in Gulf fish requires an understanding of which sources are the most important for MeHg bioaccumulation in fish. This involves determining:

- The sources of mercury to the Gulf
- Where and at what rate inorganic mercury is converted to MeHg by naturally occurring bacteria
- How MeHg cycles and bioaccumulates through the marine food web

While mercury data are limited for the Gulf, a screening-level model has been used to examine this question. Mercury cycling and bioaccumulation has been simulated by the Navy Coastal Ocean Model, coupled to the Gulf of Mexico Dynamic Mercury Cycling Model, previously used for USEPA-funded pilot mercury TMDLs in Florida and Wisconsin.

The FDEP funded initial runs of both models and has received U. S. Department of Commerce National Oceanic and Atmospheric Administration funds for research on (1) MeHg exposure to Gulf states' residents from Gulf fish, (2) total and MeHg inputs to the Gulf from rivers, and (3) Gulf fish trophodynamics.

REGIONAL SULFUR MASS BALANCE STUDY

The objectives and methods of the Regional Sulfur Mass Balance Study are described in the 2010 SFER. Thus far, three separate years have been investigated in mass balance calculations: a high precipitation year (2004 [556 cm]), a drought year (2007 [393 cm]), and an intermediate scenario (2003 [472 cm]). To date, the major findings are as follows:

- Canal transport is the largest TS mass transfer mechanism for each land-use area.
- Total sulfur source/sink characteristics vary considerably for each area per year, particularly for WCA-1 and the EAA.
- For the WCAs, the smallest total sulfur mass transfer mechanisms are total sulfur biogenic emissions and atmospheric deposition.
- Agricultural sulfur applications and total sulfur release through soil oxidation are similar in mass transfer magnitude for the EAA during years with higher precipitation.
- Lake Okeechobee shows the least variation in source/sink characteristics.

The next steps of the study are to (1) include the years 2000, 2001, 2002, 2005, 2006, 2008, and 2009 in mass balance calculations, (2) further explore biogeochemical total sulfur oxidation and reduction processes using chloride mass balance data, (3) investigate the source for sulfur that contributed to the high sulfate concentration at sampling locations, and (4) further explore sulfur source delineation for the South Florida ecosystem.

SOUTH FLORIDA MERCURY HOT SPOT STUDY: DATA COLLECTION PHASE

This study consists of sampling multiple biogeochemical parameters within porewater, surface water, sediment, mosquitofish, and periphyton at locations that exhibit contrasting fish mercury levels (see **Figure 3B-15**). Future data evaluation will involve statistically comparing parameter levels between selected locations to help identify the processes causing the large differences in fish mercury levels. Potential environmental factors could include differences in porewater carbon quantity and quality, sediment sulfur speciation levels, and sediment phosphorus levels. Two sites (ENR302 and WCA2F1) selected for data collection have demonstrated relatively low mercury concentrations in several fish species for the POR (1998–2010) [average levels range from 0.006–0.010 ppm in sunfish and 0.016–0.172 ppm in LMB (Axelrad et al., 2008; Gabriel et al., 2009)]. Sites WCA2U3 and CA315 were selected for relatively high mercury levels in all fish species for the POR (1998–2010) [average levels range from 0.175–0.324 ppm in sunfish and 0.418–0.997 ppm in LMB (Axelrad et al., 2009; Gabriel et al., 2009)]. Results and discussion are anticipated for inclusion in future SFERs.

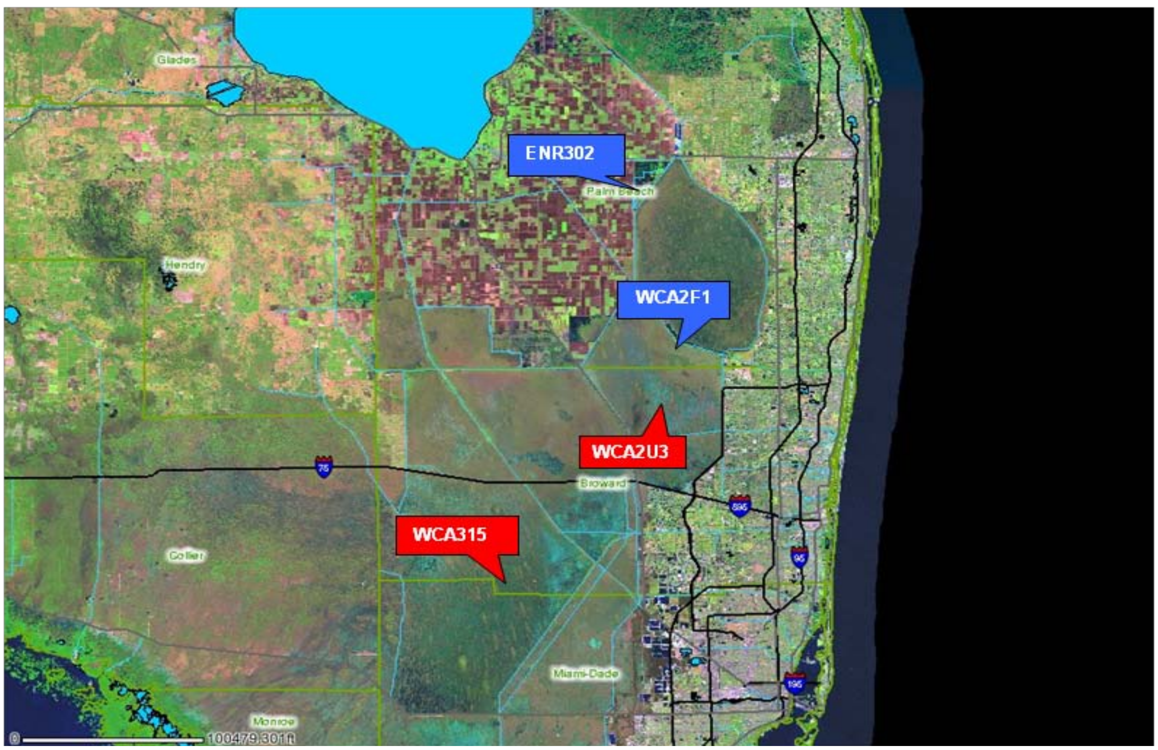


Figure 3B-16. Sampling locations within WCA-2, WCA-3, and STA-1W. Red boxes indicate high fish mercury concentration areas and blue boxes indicate low fish mercury concentration areas.

EVALUATION OF SULFUR IMPACTS IN SOUTH FLORIDA WETLANDS

The *Evaluation of Sulfur Impacts in South Florida Wetlands* is a three-year project planned for completion in 2011. The principal objectives are to determine the effects of elevated water column sulfate levels on phosphorus cycling and vegetation health in natural wetlands and the STAs. This study is detailed in 2010 SFER – Volume I, Appendix 3B-2, with the results of the first set of lab incubations on soil slurries amended with sulfate. WY2010 results are presented here.

The following sections summarize the results of field monitoring and laboratory experiments performed to assess the effects of elevated water column sulfate levels on phosphorus release from soils collected from unimpacted and impacted (with respect to sulfur) South Florida wetlands. Updates on other research platforms, including field-scale mesocosms, intact laboratory core incubations, and chemical gradient analyses in STAs, are also presented.

Porewater Concentrations and Soluble Reactive Phosphorus Release from Intact Soil Cores in the STAs

This task comprised two major efforts. The first was a field study where porewater equilibrators ("peepers") were deployed on one occasion in the central flow paths of STA-5, Cells 2A and 2B, and STA-3/4, Cells 2A and 2B, and on three occasions in STA-2, Cell 1 (**Figure 3B-16**).

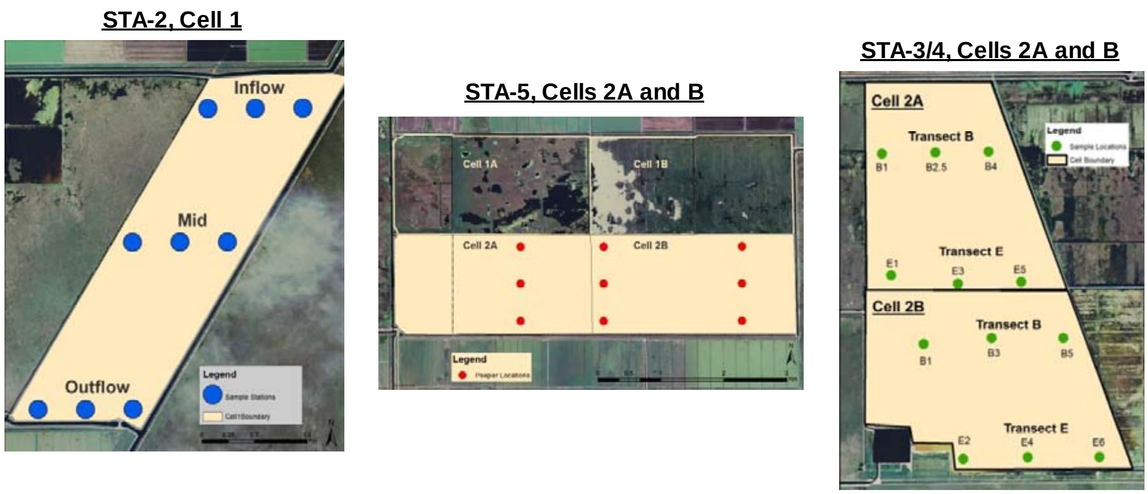


Figure 3B-16. Porewater measurement locations within the STAs.

The second effort entailed six-week lab incubations of intact soil cores collected from the porewater measurement locations. Duplicate cores from each sampling location were flooded with unamended (typically low sulfate) water from the STA flow path. Two additional cores were amended with sulfate at a concentration comparable to the highest levels observed for each STA flow path over a five-year period (2004–2009). All of the field collection and laboratory experiments for this task have been completed, and final data analyses are under way.

Preliminary findings are:

- For STA-2, Cell 1, and STA-3/4, Cells 2A and 2B, field-measured porewater soluble reactive phosphate (SRP) levels and Fickian diffusion rates from the soils to the overlying water generally were highest for the soils nearest to the inflow culverts. By contrast, porewater SRP and diffusion rates were higher along the outflow transect of in STA-5, Cell 2B, than for the mid- and inflow-transects of the flow path. A comparable spatial trend in SRP release was also observed for the intact soil cores that were incubated in the laboratory for six weeks.

- For STA-2, Cell 1 (sampled on three occasions), porewater chemistry varied in response to seasonal and antecedent hydrologic conditions. During the June 2009 deployment, performed after a prolonged drydown–reflooding event, sharply elevated sulfate, SRP, and dissolved organic phosphorus concentrations were observed along the mid-cell transect. Porewater sulfide levels were generally low at this time for this sampling location.
- No correlation was found between porewater sulfide and SRP concentrations in soil cores retrieved from STA-2, Cell 1, and STA-3/4, Cells 2A and 2B; very weak correlations ($r^2 \leq 0.23$) were found between porewater sulfide and porewater SRP concentrations in soil cores retrieved from STA-2, Cell 1, and STA-3/4, Cells 2A and 2B, at the end of a six-week wet incubation; a stronger correlation ($r = 0.57$) was observed in soils from STA-5, Cells 2A and 2B.

Phosphorus Mobilization and Plant Toxicity Effects in Mesocosms Amended with Sulfate, Calcium and Alkalinity

Three mesocosm platforms have been constructed to address the effects of sulfate amendments on phosphorus mobilization and plant toxicity. Two experiments are being conducted at the Port Mayaca lock, adjacent to Lake Okeechobee. The first study tests the potential toxicity of sulfate amendments to emergent (cattail and sawgrass) and submerged [southern naiad (*Najas guadalupensis*)] plants. Four groups of triplicate containers containing each plant type are being fed Lake Okeechobee waters. Two groups are receiving waters with ambient sulfate levels of ~ 40 ppm. The others are being fed lake waters spiked to a sulfate concentration of ~ 90 ppm. One set of ambient-sulfate tanks and one set of high-sulfate tanks are also having the lake water pre-treated to remove available phosphorus forms (**Figure 3B-17**). Plants are harvested periodically and measurements are performed on aboveground and belowground tissues to assess potential sulfate/sulfide impacts on morphology and physiology.

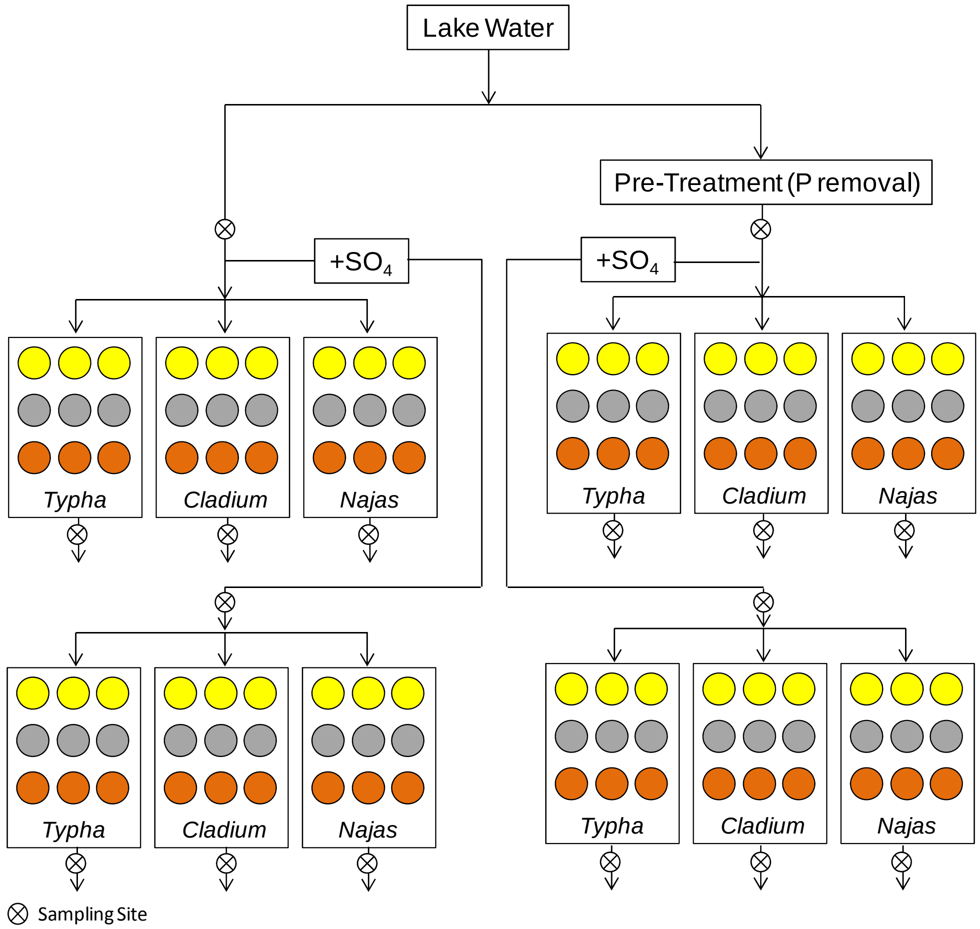


Figure 3B-17. Experimental design for the mesocosm toxicity experiments receiving sulfate amended and unamended Lake Okeechobee waters. One mesocosm group also receives pre-treated lake water. The colored circles represent containers of cattail (*Typha domingensis*), sawgrass (*Cladium jamaicense*), or southern naiad (*Najas guadalupensis*).

A second mesocosm platform at Port Mayaca is designed to test the effects of sulfate on phosphorus mobilization under a typical STA configuration (i.e., front-end emergent followed by back-end submerged communities) (**Figure 3B-18**). An additional treatment that involves increasing the calcium and alkalinity concentrations in conjunction with sulfate amendments is also being evaluated. To date, sulfate amendments (to ~ 90 ppm) to Lake Okeechobee source water have not impaired the phosphorus removal performance of the STA process trains.

Figure 3B-18. Front-end emergent (cattail) mesocosms in the STA platform at Port Mayaca (photo by DB Environmental, Inc.).

A mesocosm platform has also been deployed in a relatively pristine (low phosphorus, low sulfate) area of WCA-3A (**Figure 3B-19**). Construction of the facility has been completed, and initial vegetation and soil measurements have been performed. The mesocosms will be operated in a batch mode where outside surface water will be exchanged with the inside water on a biweekly basis. A system of underwater ports and valves will facilitate the water exchange and also minimize the hydrostatic "head" difference between the inside and outside enclosures.

During each water exchange, selected mesocosms will receive sulfate amendments to final concentrations of 12, 24, and 48 ppm. In addition, a triplicate set of mesocosms will receive 40 ppm of calcium as a final concentration, while another set of triplicate mesocosms will be amended with 40 ppm of calcium plus 48 ppm of sulfate as final concentrations. The remaining triplicate set of mesocosms will remain unamended (controls). Amendments and water exchanges began in August 2010.

Figure 3B-19. Typical ridge-and-slough vegetation communities of floating periphyton (left) and floating periphyton interspersed with sawgrass and spikerush (*Eleocharis* spp.) (right) in WCA-3A mesocosms (photo by DB Environmental, Inc.).

MERCURY AND SULFUR IN SOUTH FLORIDA WETLANDS WORKSHOP

Organized by the SFWMD, FDEP, and USGS, the Third Annual Workshop on Mercury and Sulfur in South Florida Wetlands was held on February 2, 2010. In attendance were representatives from USGS, NPS, USEPA, FDEP, Smithsonian Institute, Aqua Lux Lucis, Inc., University of Florida, DB Environmental, Inc., and Syracuse University. The purpose of this workshop was to discuss research conducted since the second annual workshop related to mercury and sulfur biogeochemistry and ecological effects in South Florida wetlands. This workshop was intended to support activities under the SFWMD's Sulfur Action Plan, the USGS South Florida Ecosystem Program, and the FDEP South Florida Mercury Science Program. Through these programs, the three agencies investigate the effects of elevated mercury and sulfur levels throughout the Greater Everglades with research emphasis placed on mercury and sulfur interactions, internal eutrophication (sulfate-induced nutrient release from sediments), sulfide toxicity, agricultural applications of sulfur, and sulfur mass balance. Another workshop is planned for June 2011.

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